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The impact of halogen free phosphorus, inorganic and nitrogen flame retardants on the toxicity and density of smoke from 10 common polymers

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Abstract

The toxicity and density of smoke from 10 commonly used commercial polymer types was studied using the European railway standard EN 45545-2. This test method was chosen because it reflects the current state-of-the-art in assessing the hazards of smoke in bench-scale test scenarios (not because of a specific link to railway applications). The study involves 72 commercially relevant formulations provided by 12 industrial companies. Polymers studied include PE, PP, PC, PA6, PA66, u-PVC, p-PVC, PU, PIR, and epoxy resins. Reference samples as well as samples containing halogenated and Phosphorus, Inorganic or Nitrogen based Flame Retardants (PIN FRs) were tested according to the French tubular furnace method (NF X 70-100) to evaluate their smoke toxicity at 600°C and according to ISO 5659-2 at 50 kW m^{-2} with Annex C of EN 45545-2 to evaluate their smoke density as well as toxicity at 4 and 8 min. This study highlights that the measured toxicity and calculated Conventional Indexes of Toxicity (CIT_{NLP}, $CIT_{4\ min}$, $CIT_{8\ min}$), as well as maximum smoke density (Ds_{MAX}) show generally no significant increase in the presence of PIN FRs in comparison to the neat polymers. The use of intumescent FRs or hydroxide based FRs generally allows considerable smoke reduction with little impact on smoke toxicity. Bromine based-FRs were found to be detrimental to both hazards in most matrices studied here.

KEYWORDS
engineering plastic, flame retardant, polyolefin, smoke, toxicity

1 | INTRODUCTION

Plastics are used in a multitude of everyday items ranging from household appliances and furniture to building materials, electronic equipment and parts for mass transportation. However, plastics are easily flammable due to their organic nature and they are the origin of many hazards during fires. Heat, smoke and toxic gases are all threats that may cause injuries or even death if they impede exit from a confined space. In fact, smoke inhalation alone or in combination with burns causes a larger share of fire deaths and injuries than burns do.[1–3] Furthermore, the shift from natural to synthetic materials combined with their mass production and consumption has for example increased synthetic fuel load inside households as well as reduced the Required Safe Egress Time (RSET) and time to flashover.[4] Railway or subway fires such as the Channel Tunnel fires (1996, 2006, 2008, 2012, 2015), Ladbroke Grove (1999) or Kaprun fire (2000) raised awareness and became learning points for the industry regarding fire safety.[5] Following this shift as well as several accidental fires by the end of the 20th century, the firefighters' response to fire has dramatically changed. To mitigate the fire issue, new regulations and standards have also been gradually adopted by different countries. Today, the level of fire performance of products is evaluated using several criteria such as flame propagation, dripping, heat release, smoke density or smoke toxicity. Performing some or all of these measurements through fire-testing is mandatory before the sale and use of a product on a regulated market. For example, the automotive market mainly requires flame propagation tests via ISO 3795 or FMVSS 302 standards to judge the conformity of components. The European or American railway market as well as the European building market require standardized fire testing and evaluation beforehand (respectively following EN 45545-2, NFPA 130 and EN 13501-1 standards). Among the markets that evaluate smoke and its short-term toxicity, we can mention the rail, sea or air transport markets which are more demanding in this regard. Thus, plastics turned out to be a concern in fire safety due to their ubiquitous nature and flammability. The legislator provided a regulatory response to the fire risk, forcing manufacturers to pass various standardized fire tests. As a result, the addition of flame retardants became one of the key parameters to meet specific fire-performance levels and more stringent fire safety regulations.

Compared to natural polymers such as wood, leather or cotton, synthetic polymers are more flammable, but this behavior can easily be modified by including a variety of Flame Retardants (FRs). Such FRs may reduce ignitability, hinder or slow down the development and propagation of a fire or reduce its related combustion products.[6–8] However, no single flame retardant can address all fire-related scenarios and issues and pass every single national or international standard. In fact, there are for example more than 10 different standards to evaluate combustion toxicity at various stages of fire development and under different conditions.[9] Toxicity test methods include but are not limited to: Naval Engineering Standard 713 (NES 713), Boeing Safety Standard (BSS 7239), Bombardier SMP 800-C, Airbus AITM 3.0005, Annexe C of EN 45545-2+A1, EN 16989. Some of these tests represent a specific fire scenario (or fire stage according to ISO 19706) whereas others present evolving conditions.[10] Furthermore, passing a single test such as UL 94 may give a false sense of safety or performance regarding the behavior of a material to fire. Different fire safety standards for each key sector have been adopted to ensure the safety of end users. However, the strategy of using flame retardants to meet specific standards should not make us forget that fire always presents multiple hazards. Most FRs can positively impact the reaction of plastics to fire, but generally only address a few key issues among ignitability, flame propagation, dripping, heat released or smoke toxicity and density. Each plastic formulation needs therefore to meet a balance to minimize as much as possible the most-likely fire hazards and scenarios (for example, limited ignitability or flame propagation), while maintaining an acceptable release of combustion products if a fire develops.

Several studies indicate that halogenated FRs, such as decabromodiphenyl ether or polybrominated biphenyls, although very effective at reducing flammability, contribute to an increased smoke toxicity and density when burning and show various environmental and health concerns.[7,11–13] Within this family of compounds, some are listed in the Stockholm Convention as persistent organic pollutants. As such, the use of Polybrominated Diphenyl Ethers has been restricted and reduced worldwide (China, the European Union, India, Japan or the United States).[14] Extensive studies and reviews have been carried out separately on halogenated FRs or Phosphorus, Inorganic and Nitrogen Flame Retardants (PIN FRs), yet only few papers have deeply compared their behavior relative to each other, particularly regarding their performance level in terms of smoke toxicity and density.[13,15,16] PIN FRs show several advantages when compared to halogen-based FRs. They are presented as showing a low evolution of smoke, do not generate dioxins or halogen acids when burning and can sometimes be recycled more readily.[17] Inorganic fillers such as aluminium trihydroxide (ATH) show clear advantages when compared to halogen-based FRs regarding their environmental impact and generally yield less toxic gases, less smoke and emit less corrosive gases.[18] Most of the time, small scale tests such as the limiting oxygen index (LOI) or Underwriters Laboratories 94 tests (UL 94) are used to give a general idea of flammability and initial ignitability. However, smoke and toxicity evaluation from FR-samples is not systematically studied in the literature, or only secondary to heat release determination by the cone calorimeter experiment (ISO 5660-1). It is therefore important to evaluate the impact of formulations containing FRs, whether PIN FRs or halogen-based FRs, on smoke density or toxicity when compared to neat polymers.

Selecting a specific fire testing method is important for the comparison of data and fire-reaction performance. On the one hand, large-scale or intermediate scale tests such as the "Single Burning Item" (also known as SBI, described in EN 13823) are more representative of real-life fire scenarios and yield more data (i.e., smoke production, heat release, flame propagation) but are more expensive and require much more material than small bench-scale tests. On the other hand, bench-scale tests are simple to perform and used daily to screen and rank fire-performance of materials. They are well documented, but their transposition to real life fire scenarios is more problematic.[9,10] Mass transportation standards mainly use such small-scale tests for comparison of fire-performance and selection of materials. They require the combination of reduced fire growth, low heat and smoke yields, as well as low smoke toxicity. Such conditions therefore constitute a challenge as well as a barrier to entry into the rail market for many manufacturers, depending on the application of the item and nature of the plastic (example in Table 1). Thus, we decided to evaluate and compare the smoke emission features of commercial formulations following the EN 45545-2 Railway standard, which is applied since 2013 and has been revised in 2020. The framework of EN 45545-2 standard was chosen to allow easy comparison of fire performance level of different products under the same test conditions.[19] The EN 45545-2 standard advises to test products under the final thickness and conditions of use, including all layers that

TABLE 1 Typical uses of everyday plastics in the scope of EN 45545-2 in railway applications.

Plastic	Rolling stock application	EN 45545-2 Requirement number
HDPE/LLDPE	Terminal strips, electronic items, electronic covers	R22, R23
PP	Seat and table trays	R6, R21
	Tube Clamps	R22, R23, R24
PC	Non-listed items, such as case glass (<500 g interior or 2000 g exterior)	R24
Epoxy	Partitions, floors and large indoor or outdoor surfaces	R1, R7
PA6	Flexible protective sheathing	R22, R23 or R6, R9
PA66	Cables	R15, R16
PUR/PIR	Insulating material	R1, R7
Flexible PU	Seat upholstery	R21, R18
PVC	Flooring (carpets)	R10
	Piping	R22, R23
	Synthetic PVC leather (upholstery)	R21

make up the final product (i.e., paints, varnishes, textiles, protective films, glues). In this study, the conditions and materials were set up to limit the variability and quantity of tests to be performed as well as the complexity of the final analysis. The purpose of this study is not to evaluate the performance or classification of raw materials related to their final conditions of use inside rolling stock, but to compare them on an equal footing using the example of a well-established railway standard and test methods.

The goal of this study was to assess the level of performance of 72 industrial-grade samples in terms of smoke density and toxicity, following well-established testing methods from EN 45545-2 standard. The use of flame retardants in the railway sector is not trivial. In fact, EN 45545-2 generally requires products to perform well in several aspects (heat release, smoke, toxicity, flame propagation) to achieve an adequate classification. The addition of the right flame retardant may therefore allow a product to pass certain tests and implement the product in the rolling stock. On the other hand, adopting an erroneous fire-retarding strategy may worsen the results on smoke or toxicity tests and cause the product to be unclassified. Furthermore, test results are frequently confidential and there is little relevant literature on this topic. Based on standardized tests widely used in the railway industry, these results could contribute to a further deepening of the understanding of the behavior of various polymeric materials and serve as a starting point for industrial benchmarking or simulations focused on smoke or toxicity (the samples are pictured in Figure 1).

Smoke composition was studied according to two different methods of analysis in a tubular furnace (NF X 70-100) at 600°C and under the NBS smoke chamber method (ISO 5659-2) at 50 kW/m^2 coupled with a FTIR spectrometer.[20–22] The FRs evaluated here are representative of those used on a large scale such as melamine cyanurate (MC), melamine polyphosphate (MPP), ammonium polyphosphate (APP), metal hydroxides, phosphates (triethyl phosphate, 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide derivatives "DOPO"), chlorinated-FRs (tris (1-chloro-2-propyl) phosphate "TCPP", Tris(1,3-dichloro-2-propyl)phosphate "TDCPP") and brominated-FRs (decabromodiphenylethane "DBDPE", Tetrabromobisphenol-A "TBBPA") derivatives. Short-term smoke toxicity from polymers was evaluated by determining the amount of three asphyxiant gases (carbon monoxide, carbon dioxide and hydrogen cyanide) as well as five irritant gases (hydrogen chloride, bromide, fluoride, sulfur oxide and nitrogen dioxide). The long-term toxicity, including evaluation of allergens (isocyanates) and carcinogens (polychlorinated biphenyls, dioxins, furans and heavy metals) was not studied here. Smoke density as a function of time was also assessed following ISO 5659-2 and compared to reference materials without FRs. Our results highlight the importance of a well thought-out fire retardant selection and formulation to improve fire safety while maintaining an acceptable level of smoke toxicity and density.

2 | MATERIALS AND METHODS

To evaluate smoke toxicity and density from various polymers, a total of 72 commercial and non-commercial polymer samples provided by 12 industrial companies were tested according to NF X 70-100 and ISO 5659-2 methods, as well as Annexe C from NF EN 45545-2+A1:2016 standard. The NF X 70-100 and ISO 5659-2 methods are briefly explained in the following paragraphs and are described in detail elsewhere.[20,21] It should be noted that results may vary between different grades of the same type of polymer, depending on its molecular weight or the percentage of complementary additives. The nature, weight percentage loading (%wt) of flame retardants as well as tested thickness is described for each polymer in the following Table 2 and in the Supporting Information (Table S5 through Table S10). The dosage of flame retardants reflect the commercially relevant necessary loading to achieve UL 94 V0 or similar performance. Polymers which vary within the same family and were provided by more than one supplier are differentiated by an indication in brackets. No further information was shared from the suppliers regarding the exact composition of the polymers, due to industrial property rights and to the sensitive nature of this data.

The EN 45545-2 focuses on fire safety for products used in rolling stock material. It categorizes products into five classes: indoor, outdoor, furniture, electrical and mechanical. According to these categories and the final use of the product, a Requirement number (R1 to R26 based on the version used in this study) is assigned to each item. Each requirement is in turn associated with different fire tests according to the risk that the item could represent in its final use and the thermal stress (fire scenario) to which the item could be subjected in case of fire. Such tests allow to evaluate for example toxicity, heat, flame propagation or smoke density and emit a classification level (HL1, HL2, or HL3) according to the corresponding Requirement

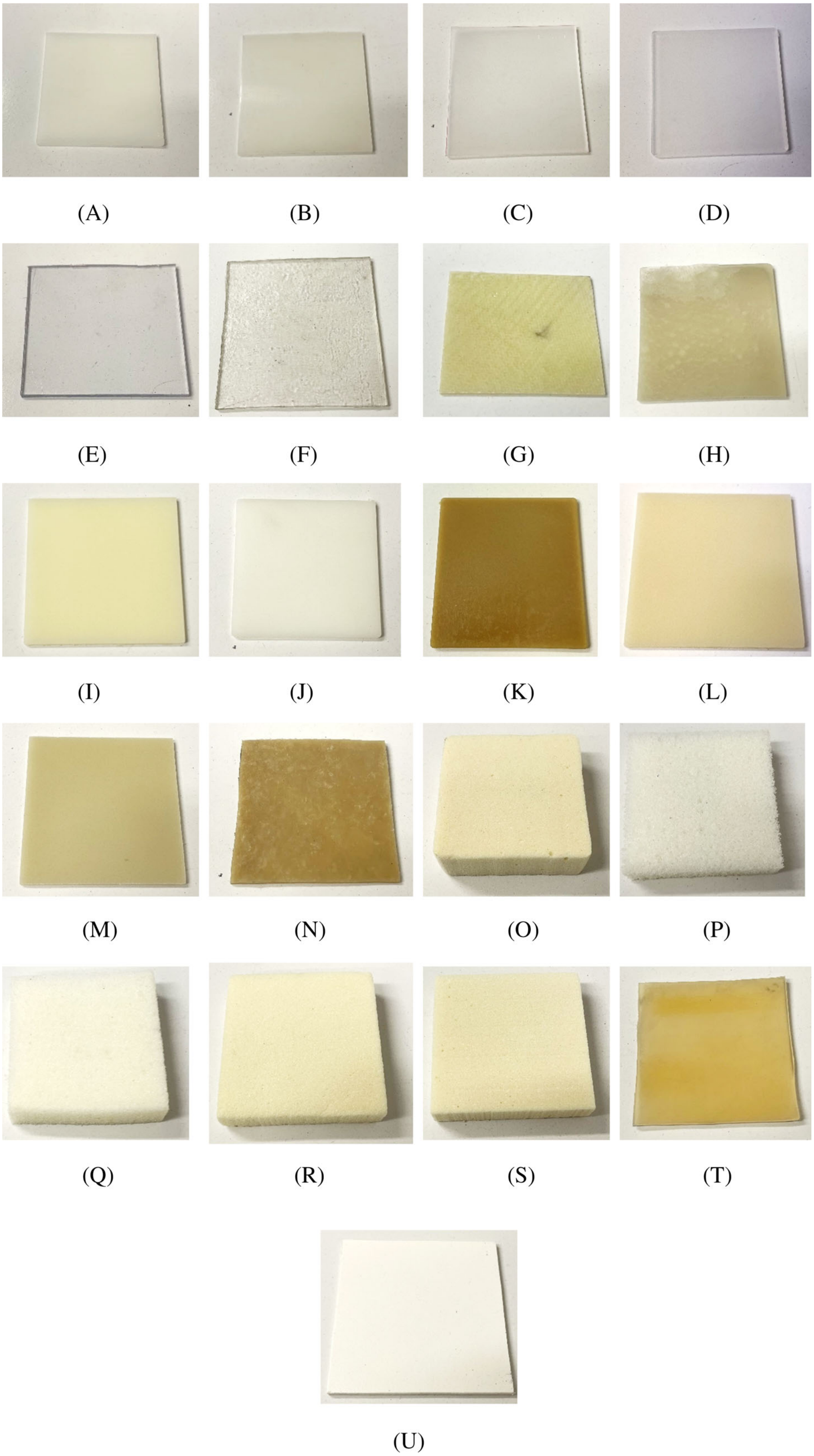

FIGURE 1 pictures of neat ISO 5659-2 polymer samples: (A) HDPE, (B) LLDPE, (C) PP (supplier 1), (D) PP (supplier 2), (E) PC (supplier 1), (F) PC (supplier 2), (G) Epoxy, (H) PA6 with 10%GF (supplier 3), (I) PA6 (supplier 4), (J) PA6 (supplier 5), (K) PA66 with 30% GF (supplier 6), (L) PA66 (supplier 7), (M) PA66 with 30% GF (supplier 7), (N) PA66 with 30% GF (supplier 8), (O) PUR, (P) flexible ether PU, (Q) Flexible Ester PU, (R) PIR (supplier 9), (S) PIR (supplier 10), (T) p-PVC, (U) u-PVC.

number based on the results obtained by the tested item. These test results account for the behavior of materials subject to specific test conditions; they do not purport to represent the only criterion for assessing the potential fire hazard posed by the product under the conditions of use. Test conditions used inside the scope of this study are detailed in the following paragraph as well as Table 3.

TABLE 2 Overview of the composition of tested samples.

Polymer matrix	Flame retardant	%Wt	Thickness (mm)
HDPE	None	-	3
HDPE	Decabromodiphenylethane and antimony(III) oxide	25%	3
HDPE	Piperazine pyrophosphate, phosphate and zinc oxide	28%	3
LLDPE	None	-	3
LLDPE	N-alkoxy amine	2%	3
LLDPE	Mixture containing hindered amines	5%	3
PP (Spl. 1)	None	-	3
PP (Spl. 1)	N-alkoxy amine	2%	3
PP (Spl. 1)	Mixture containing hindered amines	5%	3
PP (Spl. 2)	None	-	3
PP (Spl. 2)	Ammonium polyphosphate (Budit 667)	30%	3
PP (Spl. 2)	Ammonium polyphosphate (Budit 669)	30%	3
PP (Spl. 2)	Decabromodiphenylethane and antimony trioxide	30%	3
PC (Spl 1)	None	-	3
PC (Spl 1)	Brominated bisphenol-A	10%	3
PC (Spl 2)	None	-	3
PC (Spl 2)	Phosphorus-FR	20%	3
PC (Spl 2)	Br-FR	2%	3
Epoxy	None	-	2.1
Epoxy	Tetrabromobisphenol A	30%	3.2
Epoxy	Aluminium diethylphosphinate	27%	2.7
Epoxy	Ammonium polyphosphate (grade 1) containing an N-synergist	49%	3.6
Epoxy	Ammonium polyphosphate (grade 2) containing an N-synergist	27%	3.5
Epoxy	Ammonium polyphosphate	41%	1.6
PA6 + 10% glass fiber (Spl. 3)	None	-	3
PA6 + 10% glass fiber (Spl. 3)	Magnesium hydroxide	55%	3
PA6 (Spl. 3)	Brominated flame retardant and antimony trioxide	20%	3
PA6 (Spl. 4)	None	-	3
PA6 (Spl. 4)	Melamine cyanurate	10%	3
PA6 (Spl. 5)	None	-	3
PA6 (Spl. 5)	Melamine cyanurate (Budit 315)	10%	3
PA66 + 30% glass fiber (Spl. 6)	None	-	3
PA66 + 30% glass fiber (Spl. 6)	Melamine polyphosphate (Budit 610)	23%	3
PA66 + 30% glass fiber (Spl. 6)	Melamine polyphosphate (Budit 342)	23%	3
PA66 (Spl. 7)	None	-	3
PA66 (Spl. 7)	Melamine cyanurate	10%	3
PA66 + 30%GF (Spl. 7)	None	-	3
PA66 + 30%GF (Spl. 7)	Melamine polyphosphate	25%	3
PA66 + 30%GF (Spl. 8)	None	-	3
PA66 + 30%GF (Spl. 8)	Brominated polystyrene and antimony trioxide	26%	3
PA66 + 30%GF (Spl. 8)	Phosphinate	20%	3
PUR	None	-	19
PUR	Tris (1-chloro-2-propyl) phosphate	10%	19
PUR	Ammonium polyphosphate (Budit 381)	10%	19
PUR	Ammonium polyphosphate (DP Budit 382)	10%	19

(Continues)

TABLE 2 (Continued)

Polymer matrix	Flame retardant	%Wt	Thickness (mm)
Flexible ether PU	None	-	19
Flexible ether PU	Phosphonate polyol	4%	19
Flexible ether PU	Tris(1,3-dichloroisopropyl)phosphate	8%	19
Flexible ether PU	Oligomeric alkyl phosphate ester	3.5%	19
Flexible ether PU	DOPO* derivative	3.5%	19
Flexible ester PU	None	-	19
Flexible ester PU	Ammonium polyphosphate	10%	19
Flexible ester PU	Tris (1-chloro-2-propyl) phosphate	8%	19
PIR (Spl. 9)	None	-	19
PIR (Spl. 9)	Tris (1-chloro-2-propyl) phosphate	7%	19
PIR (Spl. 9)	Triethyl phosphate	7%	19
PIR (Spl. 9)	Oligomeric alkyl phosphate ester	7%	19
PIR (Spl. 10)	None	-	19
PIR (Spl. 10)	Ammonium polyphosphate	15%	19
PIR (Spl. 10)	Tris (1-chloro-2-propyl) phosphate	15%	19
p-PVC	None	-	3
p-PVC	Antimony trioxide	3.1%	3
p-PVC	Antimony trioxide and aluminium trihydroxide	3.1% + 16%	3
p-PVC	Aluminium trihydroxide	24%	3
p-PVC	2-ethylhexyl diphenyl phosphate	32%	3
p-PVC	Butylated triphenyl phosphate	32%	3
u-PVC	None	-	3
u-PVC	Antimony trioxide	2.3%	3
u-PVC	Aluminum trihydroxide	7.6%	3
u-PVC	Boehmite	7.6%	3
u-PVC	Aluminum trihydroxide	15%	3
u-PVC	Boehmite	15%	3

Abbreviations: GF, glass fiber content; Spl, supplier.

TABLE 3 Test conditions applied for ISO 5659-2+Annexe C of EN 45545-2+A1:2016 as well as NF X 70-100.

Test method	ISO 5659-2	Annexe C of EN 45545-2 (with ISO 5659-2)	NF X 70-100
Testing configuration	Horizontal	Horizontal	Horizontal
Test time	10 min	10 min	20 min
Irradiation	50 kW/m^2 without pilot flame	50 kW/m^2 without pilot flame	600°C
Burning atmosphere	Ambient air (closed chamber, no air renewal)	Ambient air (closed chamber, no air renewal)	Synthetic air (20% O_2 + 80% N_2)
Measured parameters	Smoke density	CO, CO2, HCl, HBr, HF, HCN, SO2, NOx concentrations at 4 and 8 min (in mg per m^3)	CO, CO2, HCl, HBr, HF, HCN, SO2, NOx yields (in mg per gram of burnt material)
Software	Smokebox/omnic	Smokebox/omnic	Servomex2 hyperterminal
			Chromeleon version 6.80 SR10 Build 2818

2.1 | Tubular furnace test method (NF X 70-100)

The composition of combustion gases was studied according to the tubular furnace method (NF X 70-100) at 600°C. The French NF X 70-100 method was developed to quantify the fire toxicity of gases emitted from materials used in railway rolling stock. It was mainly used in conjunction with the French railway NF F 16-101 standard and NF X 10-702 (French smoke chamber test) for smoke hazard classification (F classification). The NF X 70-100 standard was later reimplemented within the framework of EN 45545-2 for small items classification (R22 and R23 from EN 45545-2+A1:2016). This method is straightforward with a relatively simple equipment and steady operating conditions (air flow, temperature, etc.).

The static tube furnace method is performed on a small sample put in a crucible (1 g for polymers or 0.1 g for low-density materials, i.e., PUR and PIR foams). The tube is inserted into the middle of a silica furnace (60 mm diameter) and thermally decomposed for 20 min under a synthetic air atmosphere made of 20% oxygen and 80% of nitrogen flowing at 2 L min^{-1}. Furnace temperatures are usually adjusted at either 400, 600, or 800°C depending on the desired flaming conditions (oxidative pyrolysis, well ventilated or under-ventilated combustion conditions respectively). The temperature of 600°C was chosen in the context of this study, following relevant EN 45545-2 and NF F 16-101 indications. At this temperature, the sample may pyrolyze or ignite with a slow rate of burning and it is admitted that these conditions generally correspond to well-ventilated flaming. Such conditions may nevertheless evolve depending on the combustion kinetics and nature of the tested sample. As such, it is still difficult to precisely attribute an ISO fire development stage to this test. In this regard, steady-state tube furnace methods such as ISO TS 19700 might be more appropriate for controlled burning under known, steady-state fire conditions (equivalence ratio and temperature).[9] However ISO 19700 is limited in its applicability to homogeneous thermoplastics. In the context of this study, the NF X 70-100 method was selected because it is widely used to evaluate European railway products and easily performed. The 600°C temperature is employed inside the EN 45545-2 railway standard to evaluate smoke toxicity from small products such as doorknobs, gaskets, electrical boxes, or cup holders and was adopted accordingly. The test conditions employed for each material do not necessarily reflect the reality and end use of the product or an associated fire hazard. However, testing each product under the same thickness and test conditions allows for comparison of performance between materials and their respective flame-retarding strategies.

Within the scope of this study, the NF X 70-100 test was performed to quantify the following 8 toxic gases: CO, CO_2, HCl, HBr, HF, HCN, SO_2, NO_x (i.e., NO and NO_2). The acid gases (HCl, HBr, HCN, HF, SO_2, NO_2) were trapped inside a bubbler and the resulting solutions were analyzed by ion chromatography (HCN: Dionex ICS300—HCl, HBr, HF, SO_2, NO_2: Dionex ICS2000, software: Chromeleon version 6.80 SR10 Build 2818). Gaseous HF was trapped inside a 1 mol L^{-1} standard commercial sodium hydroxide solution (AVS TITRINORM, supplier: VWR Chemicals). Gaseous HCl, HBr, SO_2, and NO_2 were trapped inside a 0.3% (volume/volume) diluted solution of hydrogen peroxide (Ultrapure 30% hydrogen peroxide, supplier: Carlo Erba Reagents). Gaseous HCN was trapped inside a diluted 0.1 mol L^{-1} sodium hydroxide solution. Carbon monoxide, carbon dioxide and nitrogen oxide were quantified by non-dispersive infrared spectroscopy (Servomex 4200, software: Servomex2 Hyperterminal). The amount of each gas measured for each sample is reported in the Supporting Information as a yield in milligram of emitted gas per gram of burnt material (mg g^{-1}).

TABLE 4 Reference concentrations of gaseous components (from EN 45545-2 Annexe C).[22]

Gaseous component	Reference concentration([mg m^{-3})
CO_2	72 000
CO	1380
HBr	99
HCl	75
HCN	55
HF	25
NO_x	38
SO_2	262

The measured gas contents were compared with critical concentrations corresponding to the maximum concentration that an individual can withstand for 30 min without irreversible biological damage. These values are presented in EN 45545-2 Annexe C and included in the following Table 4. They are based on the IDLH values (Immediately Dangerous to Life or Health) published by the National Institute for Occupational Safety and Health (NIOSH) (1997 version). Those values are recognized as immediately dangerous concentrations of exposure for workers. Based on these values and the results obtained on each sample, the conventional index of toxicity for non-listed products (CIT_{NLP}) is calculated with the following formula (excerpt from EN 45545-2, Annexe C)[22]:

$$CIT_{NLP} = \frac{450g}{150m^3 \times N} \times \sum_{i=1}^{i=8} \frac{Y_i}{C_i}$$

Where the model of combustion is an average of 450 g of material burning inside a 150 m^3 volume. N is a reduction factor with a value of 3 representing the assumed fraction of the toxic potency which is realized in a fire. Y_i is the yield at the i^{th} gas in mg g^{-1} in the tubular furnace according to NF X 70-100-1; C_i is the IDLH (immediately dangerous to life and health) reference concentration of the i^{th} gas in mg m^{-3}. The 150 m^3 volume is assumed to correspond to the average rolling stock cars under operation. This formula does not consider effects of stratification, dispersion outside the vehicle, ventilation and/or condensation on cold surfaces. The most restrictive value of CIT_{NLP} inside the EN 45545-2 is 0.75, which means that CIT_{NLP} values inferior to this threshold could hypothetically qualify a product for railway applications. Only one sample of each polymer was analyzed, the data scattering was not quantified in this study. The use of other toxic potency formulas such as the FED or the FEC or the determination of equivalence ratios (linked to specific fire stages) was not considered as it would require knowledge of oxygen concentration, which was not measured in this study. The exact smoke composition for each sample was not the focus of this study, but rather to give an insight of the behavior of a population of samples with different flame retardants under the same test conditions.

2.2 | European smoke chamber test (ISO 5659-2 + Annexe C of EN 45545-2)

The evaluation of both smoke density and toxicity (4 and 8 min) was performed following the ISO 5659-2 with EN 45545-2, Annexe C. Two samples were tested in each case and the worst result out of the two tests was selected and presented here. All plastic samples were tested at the same thickness of 3 mm (for PE, PP, PC, PA6, PA66, u-PVC, and p-PVC) whereas foams were tested at 19 mm (PUR, PIR foams) to allow easier results comparison. Epoxy samples on the other hand were provided at various thicknesses by the suppliers (industrial companies) (Table 2). Testing was performed in a NBS smoke chamber (FTT, UK—Fire Testing Technology, software: SmokeBox 4.2a) coupled with a Fourier Transform Infrared spectrometer (FTIR Nicolet 6700 spectrometer, software: OMNIC 8.3). Inside the scope of EN 45545-2, this method is either used at 50 kW m^{-2} without pilot flame to evaluate smoke production from goods with a large surface area (such as walls, doors, luggage racks or tables) or used at 25 kW m^{-2} with pilot flame (for flooring, exterior roofing, seat upholstery and non-listed products mainly). Not all materials perform better under the same configuration, it is thus possible to observe more smoke for certain materials at 25 kW m^{-2} than at 50 kW m^{-2}. We have chosen to test at 50 kW m^{-2} without pilot flame (conditions used for large products) rather than 25 kW m^{-2} with pilot flame to give complementary test conditions relative to NF X 70-100, which is rather used for small products inside EN 45545-2.

A sample of 75 × 75 mm is wrapped in aluminium foil (matt side of the sheet in contact with the sample) and placed in a sample holder exposed horizontally at 25 mm distance under a conical furnace at 50 kW m^{-2} without pilot flame for 10 min, inside a 0.51 m^3 closed compartment.[9] Intumescent samples are placed at 50 mm distance under the conical furnace, which is adjusted to reach the same irradiation level than the 25 mm distance (50 kW m^{-2}). The combustion reaction consumes the available oxygen in the chamber and fire progresses from sufficiently ventilated at the beginning to under-ventilated. Mixing of the atmosphere inside the smoke chamber is only done by internal flow, which may produce inhomogeneous burning conditions locally. As such, composition of the atmosphere and decomposition conditions (temperature, local O_2 availability) are highly dependent on the tested material. It is therefore difficult to assign a specific fire stage to these test conditions.[23] The smoke density measurement is carried out by assessing the attenuation of a white light beam inside the smoke chamber. The darkening produced by the smoke is measured as a fraction of the light intensity arriving at the photometric detector in the presence of smoke, corrected by the value corresponding to the light transmission in the absence of smoke before the start of the test. If light transmission levels are below 0.0001%, the smoke density Ds is considered as above 792 and noted as Ds > 792 which is the maximum measurable value. Each sample was weighed before and after the tests to evaluate burnt mass, which is reported in Table S11 of the Supporting Information.

The gases produced by the combustion of the sample are accumulated in the chamber. After 4 or 8 min of testing, an instantaneous measurement of the concentrations (in mg m^{-3}) of CO, CO_2, HF, HCl, HBr, HCN, NO_x, and SO_2 is performed through a probe placed inside the chamber. A fraction sample from the smoke is directed to the infrared spectrometer that allows the identification and quantification of toxic compounds. Analysis of the collected spectrum during the test allowed measurement of the concentration of gases. A measurement cell of 2 L (ZnSe, 180°C under 650 Torr pressure, flow rate of 4 L min^{-1}) was used, coupled with a 1 and 0.1 μm PTFE filters mounted in series and connected to a 2 m PTFE line heated at 180°C for sampling (30 s sampling). A Nicolet 5700 FTIR (supplier: Thermo Fisher Scientific) was used, with 4 scans per spectra (from 500 to 4200 cm^{-1} with a 0.5 cm^{-1} resolution). Prior to infrared measurements, calibration of the FTIR apparatus was performed by measuring different concentrations of gases using appropriate CO, CO_2, HF, HCl, HBr, HCN, NO_x, and SO_2 bottles (supplier: Air Products France) with known concentration and dilutions. Detection and quantification limits of the method are detailed in Table S17 from the Supporting Information.

The general conventional toxicity index CIT_G (or ITC_G as per NF EN 45545-2) is derived from the gaseous concentrations measured at 4 or 8 min and the Table 4, according to the formula:

$$CIT_G = \frac{0,51\,m^3 \times 0,1\,m^2}{150\,m^3 \times 0,004225\,m^2} \times \sum_{i=1}^{i=8} \frac{c_i}{C_i}$$

where the model is the combustion of 0.1 m^2 of product; the gaseous effluents are dispersed in 150 m^3; the volume of the test chamber is 0.51 m^3; the exposed surface of the test specimen is 0.004225 m^2. c_i is the concentration measured in mg m^{-3} of the i^{th} gas in the smoke chamber according to EN ISO 5659-2 and C_i is the IDLH reference concentration in mg m^{-3} of the i^{th} gas. CIT_G values are dimensionless. The most restrictive value of CIT_G inside the EN 45545-2 is 0.75, which means that values inferior to those could qualify the product for railway applications.

Separate non-published inter-laboratory tests gave an indication of the order of magnitude of the scattering that can be expected under ISO 5659-2 testing. The repeatability and reproducibility of the specific optical density of plastics (according to Annexe D of ISO 5659-2) are given in Table S18 from the Supporting Information. The average Ds10 results show that smoke production depends on the ease of ignition of the materials, as well as their nature, grade and thicknesses. As these tests were realized in a separate study with samples different from the ones of the current article, the repeatability and reproducibility are only given as indicative data. It should be noted from these inter-laboratory tests that some materials such as polyurethane foams are more prone to data scattering in the smoke chamber test then other standard thermoplastics such as ABS.

3 | RESULTS

3.1 | Smoke chamber results

Evolution of smoke density (Ds) as a function of time is reported individually for each tested polymer in the following paragraphs and

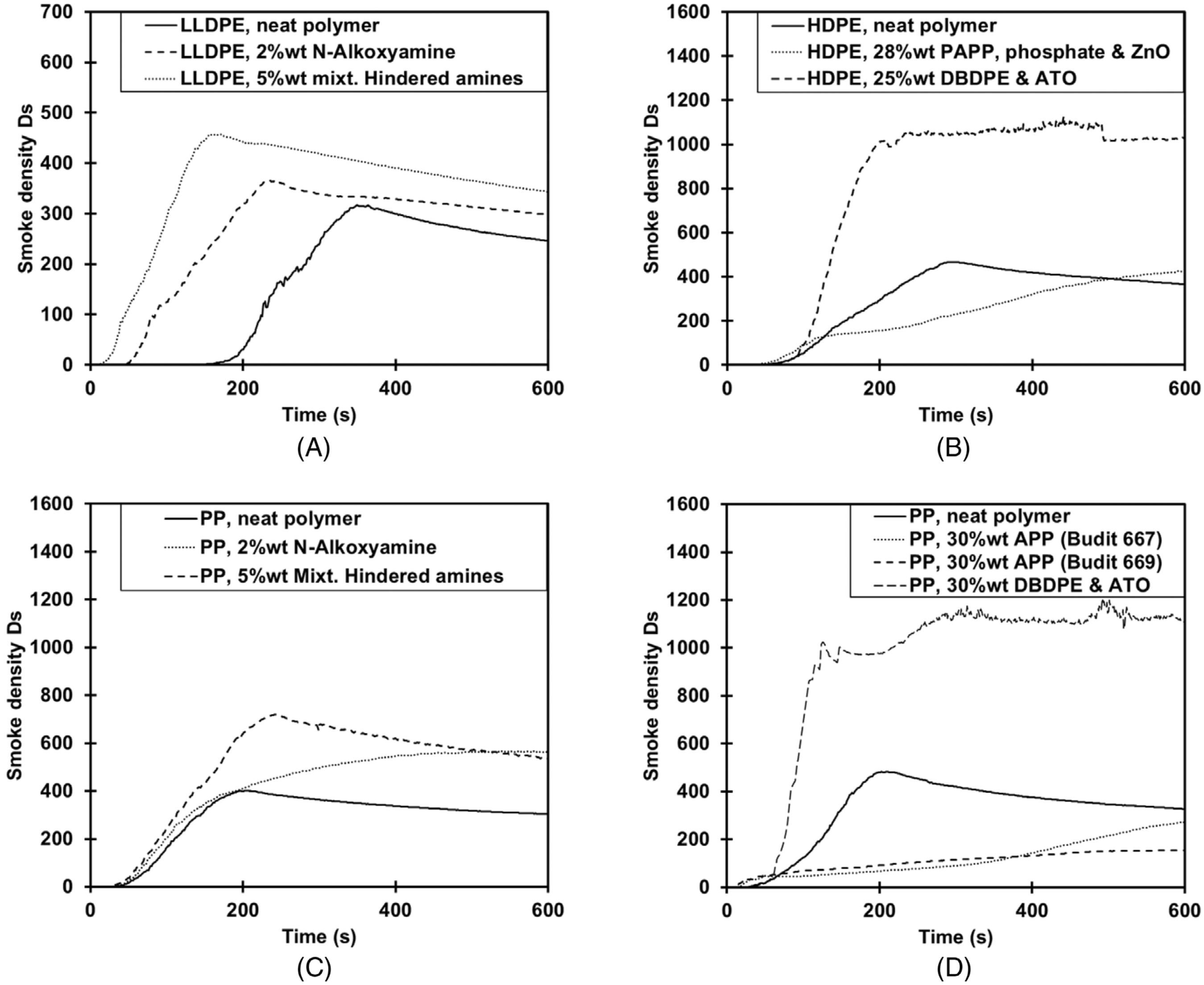

FIGURE 2 Evolution of smoke density as a function of time for (A) LLDPE samples, (B) HDPE samples, (C) PP samples (grade 1) and d) PP samples (grade 2) in ISO 5659-2 test at 50 kW m^{-2}.

figures. Individual values for maximum smoke density (Ds_{MAX}), time to maximum smoke density as well as mass loss are reported in the Supporting Information (Table S11 through Table S16).

Smoke density results for the polyolefins are presented in Figure 2 (detail in Table S11). Neat LLDPE shows a Ds_{MAX} value of 317 after 350 s, accompanied by relatively low CO and CO_2 emissions at 4 or 8 min of test time (4 min: 3804 and 139 mg m^{-3} respectively, 8 min: 8706 and 226 mg m^{-3}, respectively). The inclusion of N-alkoxy amine or hindered amines has a slightly negative impact on smoke production: both lead to shorter times to peak smoke density and higher Ds_{MAX} values in LLDPE (366 at 242 s and 510 at 254 s, respectively). Furthermore, inclusion of 5%wt hindered amines in LLDPE led to the detection of HCN and NOx by FTIR. These effluents were not quantified in the 2%wt N-alkoxyamine LLDPE sample, due to their low concentrations. The inclusion of amine-based FRs in LLDPE therefore appears to accelerate the combustion kinetics in the smoke chamber at 50 kW m^{-2} and does not improve smoke or toxicity performance. Neat HDPE shows both a higher smoke density and toxicity than neat LLDPE, with a Ds_{MAX} value of 467 at 299 s and CIT values of 0.05 and 0.07 at 4 and 8 min, respectively. Smoke emission is reduced by the inclusion of a 28%wt mixture of Piperazine pyrophosphate (PAPP), phosphate and zinc oxide in HDPE (Ds_{MAX} 427 after 600 s of test), although at the cost of additional NO_x emissions in the gas phase. Inclusion of decabromodiphenylethane (DBDPE) and antimony(III) oxide (ATO) in HDPE drastically increases smoke production with Ds values above 792 after 166 s and peak around 441 s. The same behavior is observed in polypropylene (PP) mixed with DBDPE and ATO, with Ds values above 792 after 107 s. This Br-FR also increases CO production in both PP and HDPE. Neat PP shows Ds_{MAX} values between 402 and 483 around 200 s of test time depending on the considered polymer grade. Inclusion of APP clearly reduces smoke production in PP, as can be seen on Figure 2D. N-alkoxy amine and hindered amines in PP show however no positive impact on smoke production or smoke toxicity in PP and slightly increase Ds_{MAX}

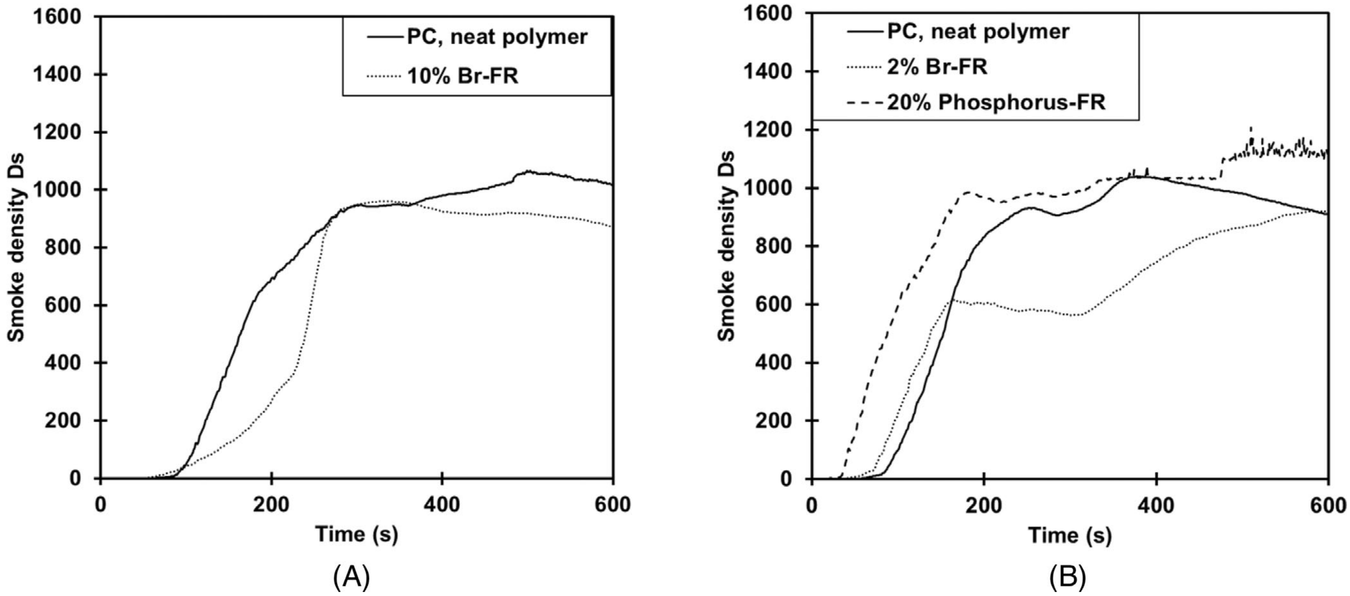

FIGURE 3 Evolution of smoke density as a function of time for PC samples (A) grade 1 and (B) grade 2 in ISO 5659-2 test at 50 kW m^{-2}.

values (respectively up to 567 and 721). Intumescent FRs such as APP or PAPP seem therefore to play a significant role in smoke reduction for polyolefins, whereas amines or Br-FRs show a neutral to detrimental impact on smoke production, as well as a neutral impact on smoke toxicity measured at 4 and 8 min of ISO 5659-2 test time.

Results for polycarbonate samples are shown in Figure 3 (detail in Table S12). Polycarbonate is known for its intermediate smoke production compared to other resins such as polyolefins, due to its aromatic backbone and its high thermal stability. PC samples tested inside the scope of this study show fast combustion kinetics and high smoke density values, regardless of their composition. Inclusion of Br or P-based FRs show a limited impact on smoke production. Furthermore, inclusion of FRs in PC showed no drastic improvement on $CIT_{4\ min}$ and $CIT_{8\ min}$ values, with similar CO and CO_2 yields than neat polymer.

Epoxy samples tested in this study were provided at several thicknesses, results should therefore be compared with caution (Figure 4, Table S13). Epoxy was found to mainly produce CO, CO_2, HCN, and NO_x through the FTIR smoke chamber measurements. Neat epoxy produces high amounts of smoke and shows a Ds_{MAX} value >792 after only 140 s of the test and a peak value at 181 s. These results are consistent with a previous study reporting a 797 Ds_{MAX} value for neat epoxy (3 mm) at 50 kw m^{-2}.[24] Although tested at higher thicknesses than the reference sample, neither aluminum diethylphosphinate nor tetrabromobisphenol A appear to reduce smoke emission in epoxy. However, all mixtures containing APP yielded less smoke (Ds_{MAX} values between 227 and 591) as well as lower gaseous toxicant concentrations (Supporting Information) and showed a slower smoke production kinetic compared to neat epoxy. This result could be ascribed to both the effect of increased sample thickness as well as the incorporation of an intumescent FR.

Polyamide 6 and Polyamide 66 smoke density results are shown in Figure 5 and Table S14. Neat PA6 produces less smoke (Ds_{MAX} values between 188 and 424) at 50 kW m^{-2} than PA66 (Ds_{MAX} values between 511 and 616), but both materials show maximum smoke density values between 250 and 400 s test times on average. Both types of polyamides (PA6, PA66) mainly emit NO_x under the smoke chamber test conditions at 4 and 8 min, followed by HCN, CO and CO_2. Melamine cyanurate was found to increase smoke emissions in PA6 and PA66. Nevertheless, MC decreased NO_x concentrations in all cases compared to neat polyamides at 4 and 8 min of test time in the smoke chamber (Supporting Information). Br-FRs combined with ATO were found to be detrimental to smoke emissions for both PA6 and PA66, with Ds_{MAX} values >792 after a short period of time (126 s in PA6, 182 s in PA66). Furthermore, PA6 with the inclusion of 20%

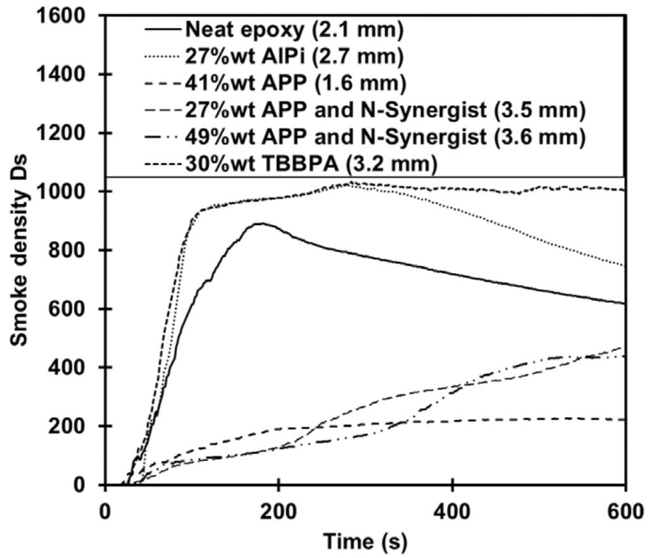

FIGURE 4 Evolution of smoke density as a function of time for epoxy samples in ISO 5659-2 test at 50 kW m^{-2}.

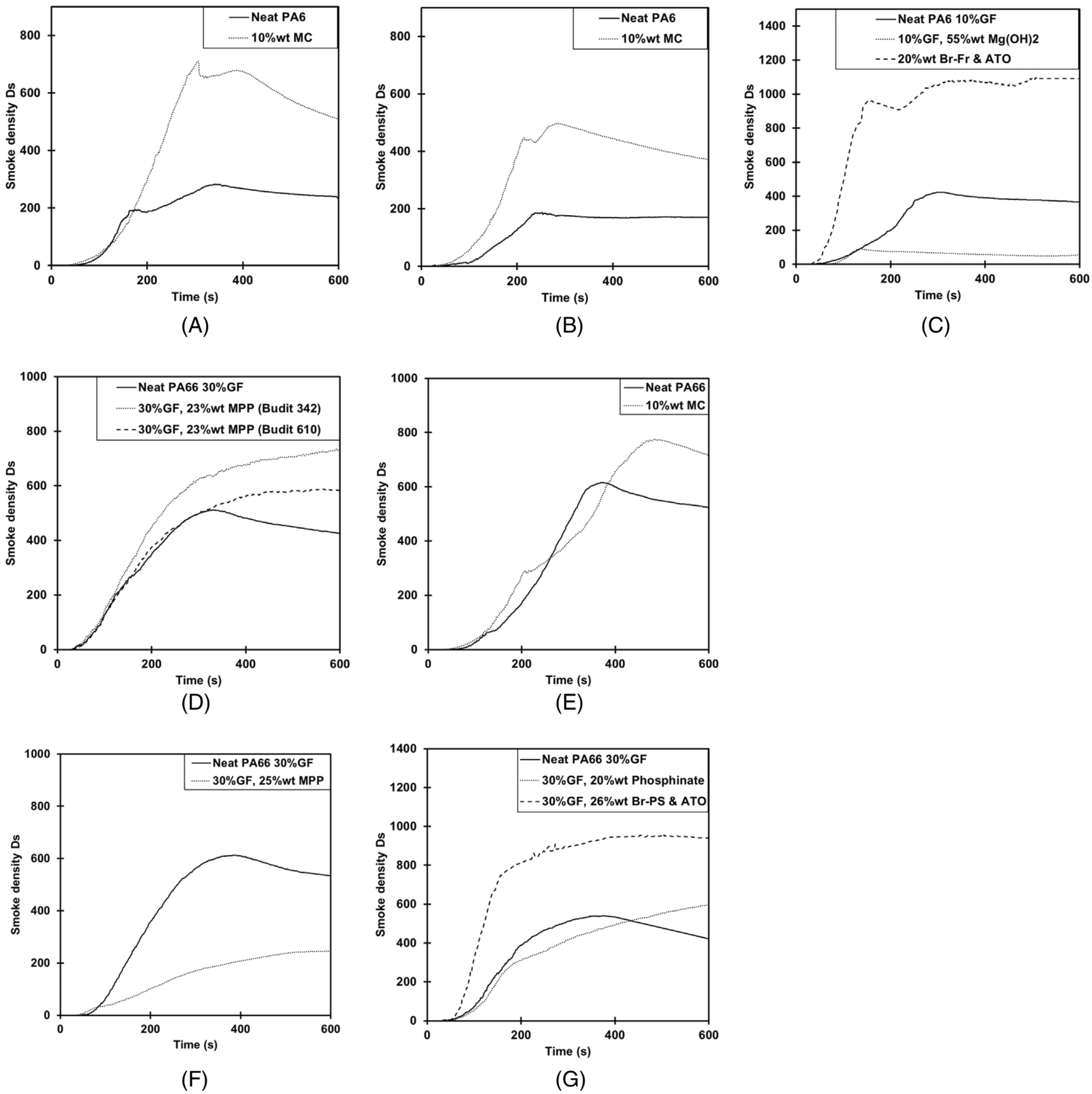

FIGURE 5 Evolution of smoke density as a function of time for (A–C) PA6 samples (grade 1, 2, and 3, respectively), (D) to g) PA66 samples (grade 1, 2, 3, and 4, respectively) in ISO 5659-2 test at 50 kW m^{-2}.

wt Br-FR and ATO showed increased NO_x concentrations at 4 and 8 min. The addition of 23%wt MPP or 20%wt phosphinate in PA66 did not yield significant improvements regarding smoke production but entirely removed NO_x from smoke at 4 and 8 min. Among FRs tested in PA6, only magnesium hydroxide was found to significantly decrease smoke emissions to very low amounts (Ds_{MAX} at 92 after 166 s) with little effect on $CIT_{4\ min}$ and $CIT_{8\ min}$ values. Overall, Br-FRs yielded the worst results in polyamide, followed by melamine cyanurate. MPP and phosphinate FR additives were found to have a neutral to small positive impact on smoke emissions from polyamide, whereas magnesium hydroxide was the only FR which showed important smoke reduction with little effect overall on smoke toxicity.

All untreated polyurethanes analysed in this study showed a maximum smoke density value after only 50–100 s of testing (Ds_{MAX} values around 200, Figure 6A–F, Table S15), regardless of their rigid or flexible nature and their composition (ether-based, ester-based or isocyanurate). Although polyurethanes are usually tested at 25 kW/m^2 following R21 from EN 45545-2 as "sandwich products" (i.e., assembled with a textile and possibly a fire barrier), we chose to test them at 50 kW/m^2 to remain consistent with the rest of the study and be able to make

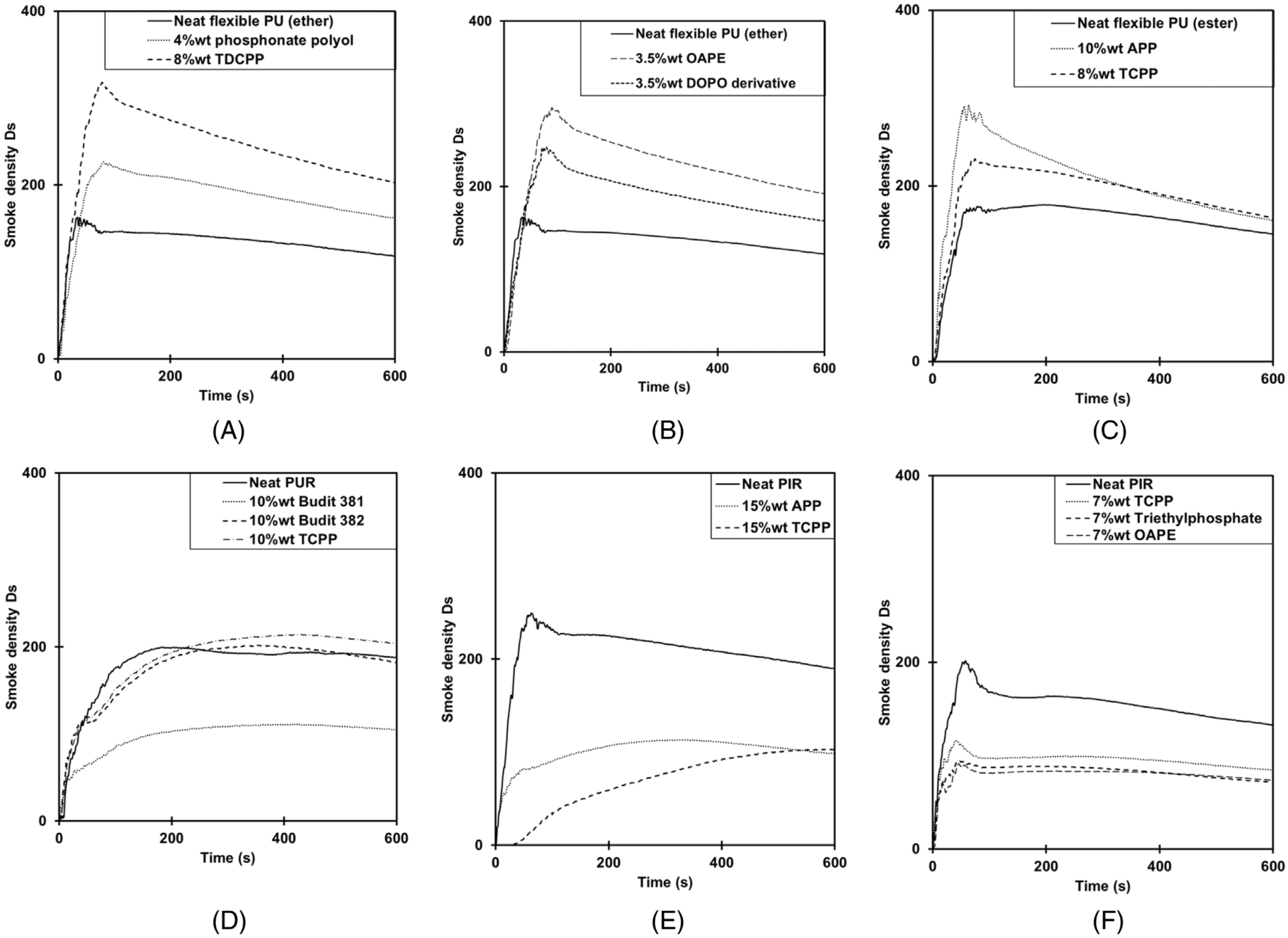

FIGURE 6 Evolution of smoke density as a function of time for (A) ether-based flexible PU samples (grade 1), (B) ether-based flexible PU samples (grade 2), (C) ester-based flexible PU samples, (D) PUR, (E) rigid PIR samples (grade 1) and (F) rigid PIR samples (grade 2) in ISO 5659-2 test at 50 kW m^{-2}.

comparisons with other types of polymers. In addition, polyurethane can also be subjected to intense thermal stresses if a fire develops on the rear side of a seat and pierces through. These results underline the high flammability of this type of polymer under high thermal stress. Polyurethanes will mainly emit CO, CO_2, HCN, and NO_x at medium concentration levels when burning under these conditions, as can be seen in the Supporting Information. Most FRs used in flexible PU showed no clear improvement on smoke production, with Ds_{MAX} values varying between 227 and 318 versus 163 to 178 in untreated samples. These results contrast with those obtained on rigid PUR and PIR, where the same FRs play a more important role in smoke reduction. For example, TCPP used in flexible ester-based PU at 8%wt loading slightly increases smoke production (Ds_{MAX} of 231 versus 178 for the neat polymer), whereas it decreases smoke production by half in PIR when used at 7%wt or 15%wt loadings (Ds_{MAX} of 116 and 103 versus 201 and 250 for the neat PIR). APP also showed the same kind of behavior and yielded better results in PIR than in flexible PU. Comparison of $CIT_{4\ min}$ and $CIT_{8\ min}$ values in polyurethanes indicates that FRs seem to have little to no effect on toxicants concentrations (Supporting Information) in the smoke chamber test.

Results of ISO 5659-2+Annexe C of EN 45545-2 for PVC samples are shown in Figure 7 and in the Supporting Information (Table S16). Smoke is produced more quickly and in higher quantities in plasticized-polyvinylchloride (p-PVC) than in unplasticized-polyvinylchloride (u-PVC). The negative effect of plasticizer on smoke production has already been documented and our results further confirm their role regarding this issue.[25] Although ATO and ATH slightly reduce smoke emissions in p-PVC, their effect is rather limited in an already high smoke yielding polymer. In most cases measured HCl concentrations in the smoke chamber were also high for PVC (>1000 mg m^{-3}), except when boehmite was employed. In fact, boehmite in u-PVC revealed a drastic smoke reduction effect (Ds_{MAX} of 44 and 52 after 600 s of testing) as well as lower HCl concentrations at 4 and 8 min of testing time, compared to its neat polymer counterpart (Ds_{MAX} of 535 after 600 s). These results were also accompanied by very low weight losses (16% and 21% weight loss vs. 92% in neat u-PVC). These results indicate that less material was burned, resulting in proportionately less smoke and HCl release. To our knowledge the mode of action of boehmite is not documented at present and this result has not been recorded before. Boehmite is generally regarded as showing an intermediate FR behavior and performance between aluminum oxide and aluminum hydroxide.

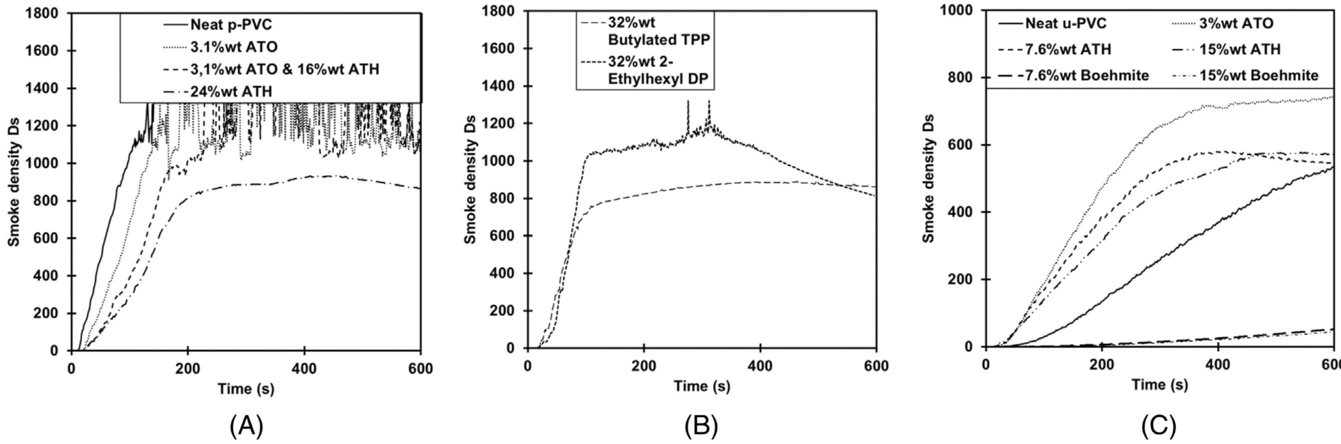

FIGURE 7 Evolution of smoke density as a function of time for (A) p-PVC samples (grade 1), (B) p-PVC samples (grade 2), (C) u-PVC samples in ISO 5659-2 test at 50 kW m^{-2}.

3.2 | Tubular furnace results

Results from smoke toxicity evaluation by the NF X 70-100 method are shown in Figures 8–13. The individual gas yields (in mg g^{-1}) for each tested sample can be found in the Supporting Information material (Table S5 through Table S10). CIT_{NLP} values calculated according to Annexe C of EN 45545-2 were used as a basis of comparison between samples: the higher the value, the more harmful the gas mixture produced by the combustion of the polymer is.

Typical CIT_{NLP} values for LLDPE, HDPE and PP were found to be around 0.15 for most samples (far below the most restrictive CIT_{NLP} value of 0.75 in EN 45545-2), except for APP and Br-FR samples (Figure 8). The major toxicant found in smoke emitted by polyolefins appears to be carbon monoxide, with yields varying between 80 and 171 mg emitted per gram of burnt polymer under these test conditions. Addition of Br-FRs and ATO in HDPE or PP produced high amounts of HBr in the gaseous phase (56 and 72 mg g^{-1}, respectively). This gas in the analyzed mixture predominantly contributes to toxicity and this is reflected by higher CIT_{NLP} values (0.71 and 0.80). Addition of N-based FRs in polyolefins was found to lead to HCN and NOx emissions, the amount of which is moderate and depends on the nature of the FR and its loading rate. For the polyolefins group, the composition of the effluents from combustion in NF X 70-100 test is therefore dependent on the formulation itself and smoke toxicity is not reduced by the inclusion of FRs.

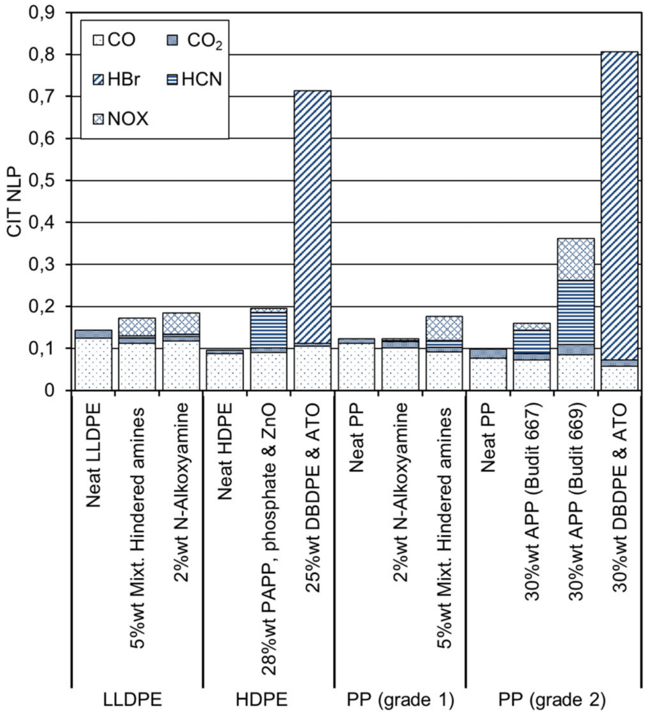

FIGURE 8 Comparison of CIT NLP values for LLDPE, HDPE and PP calculated from NF X 70-100 results.

Figure 9 shows the results obtained for polycarbonate samples. All tested samples present high CO concentrations (339–442 mg g^{-1}), which is identified as the main toxicant from smoke emitted by polycarbonate. Br-FRs are slightly detrimental to smoke toxicity evaluation and produce HBr effluents. Inclusion of 20% phosphorus-based FR proved to slightly decrease CO production and the overall toxicity of the smoke mixture (CIT_{NLP} of 0.25 vs. 0.33 for the neat polymer). However, none of the FRs in this study significantly reduced the toxicity of PC at 600°C in the tubular furnace method.

Gaseous effluents evolving from epoxy samples in the tubular furnace method were found to be mainly composed of CO, CO_2, HCN, and NO_x in varying amounts (Figure 10). It should be noted that sample thickness was not considered in NF X 70-100 testing, since a 1 g sample is taken from the material for each test. The inclusion of TBBPA yielded the expected presence of HBr in the effluents and a higher-than-average CIT_{NLP} value. Aluminium diethylphosphinate and APP showed overall little but positive effect on the toxicity of smoke. It appears however that APP mixtures promote the formation of NO_x over CO compared to the neat epoxy sample (1.68–2.58 mg g^{-1} of NO_x measured in the presence of APP, 0.16 mg g^{-1} emitted by the neat resin). Br-FRs therefore have the most detrimental impact on

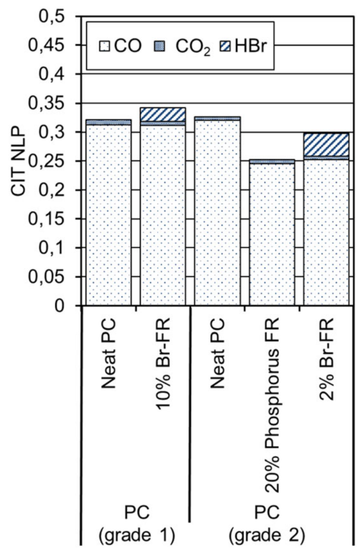

FIGURE 9 Comparison of CIT NLP values for polycarbonate samples, calculated from NF X 70-100 results.

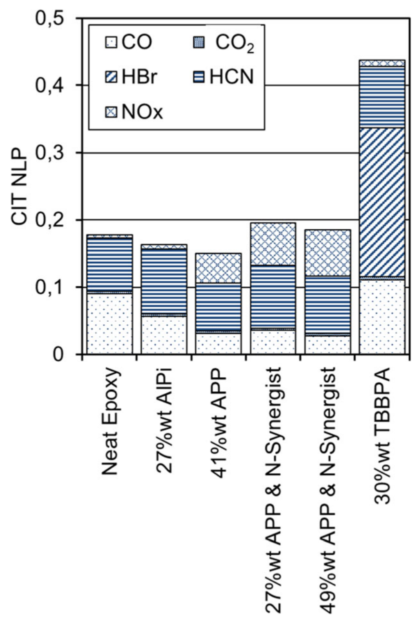

FIGURE 10 Comparison of CIT NLP values for epoxy samples calculated from NF X 70-100 results.

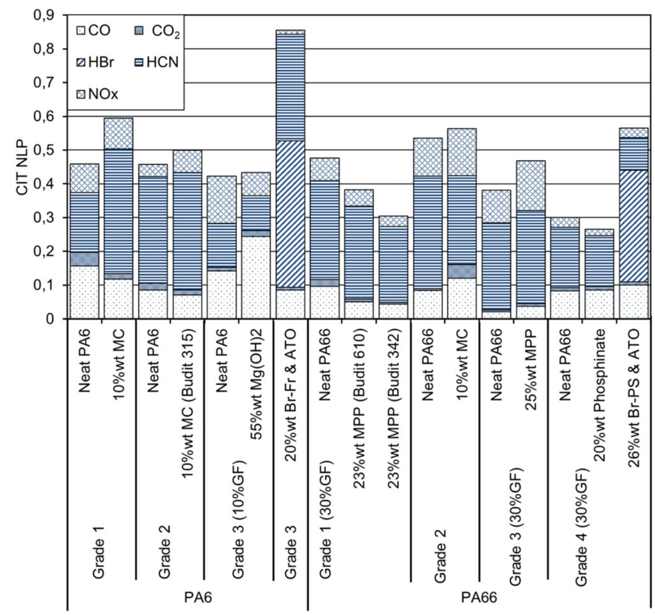

FIGURE 11 Comparison of CIT NLP values for PA6 and PA66 calculated from NF X 70-100 results.

gaseous effluents measured in epoxy samples, whereas PIN-FRs studied here showed little impact on CIT_{NLP} values.

Polyamide 6 and 66 produce significant amounts of HCN, NOx, and CO due to their nitrogen-rich content and present therefore a higher smoke toxicity than other types of polymers without nitrogen. This is reflected by CIT_{NLP} values comprised between 0.42 and 0.46 for neat PA6 and 0.30–0.53 for neat PA66. The addition of MC in PA6 or PA66 was found to be slightly detrimental to toxic effluents production. In PA6, this FR increased HCN and NOx yields and decreased CO yields (Figure 11 and Table 1 in Supplementary Information). In PA66, MC increased CO and NO_x yields and decreased HCN yields, highlighting a possibly different decomposition mechanism already mentioned in the literature.[26] Magnesium hydroxide in PA6 was found to modify the composition of the gaseous effluents to CO mainly, but the calculated CIT_{NLP} value remains in the same range as the neat polymer (CIT_{NLP} of 0.43 and 0.42, respectively). Due to their composition and mode of action, brominated FRs add HBr to the gas mixture of PA6 and PA66 and increase CIT_{NLP} values. The effect of MPP in PA66 is positive on the whole but seems to be dependent on the polymer grade, the FR considered and its loading rate. For polyamides, the addition of FRs has a very variable impact: Br-FR increases the toxicity of the gaseous effluents, MC also but to a far lower extent, MPP behavior differs in PA6 and PA66 and most other PIN FRs studied here show little impact on CIT_{NLP} values.

As nitrogen-containing polymer, polyurethanes were found to emit the same types of gaseous effluents as polyamides, mainly HCN, NOx, CO and CO_2 when burning under the tubular furnace conditions (Figure 12). All neat flexible polyurethane samples (ester or ether-based) show similar smoke compositions and CIT_{NLP} values (0.33). Rigid PUR and PIR on the other hand show higher smoke toxicities than flexible PU. Inclusion of TCPP or TDCPP in polyurethanes produces small amounts of HCl (between 2.4 and 4.5 mg g^{-1}). Furthermore, TCPP appears to behave differently in flexible PU foams than in rigid PU foams (PUR / PIR). TCPP was indeed found to increase HCN yields in both PIR (from 15 to 24 mg g^{-1}) and PUR (from 6.2 to 10.2 mg g^{-1}), and gave a CIT_{NLP}-value above the 0.75 mark in PUR, whereas it had almost no influence on HCN yields in flexible PU (8.7 to 9.4 mg g^{-1}). The addition of APP produces varying results depending on the considered matrix: in PUR, APP was found to slightly reduce smoke toxicity whereas the opposite was observed in PIR and flexible PU. Oligomeric alkyl phosphate esters and phosphonate polyol showed almost no impact on CIT_{NLP} values. Reduced CO yields were observed in the case of triethylphosphate in PIR and DOPO in

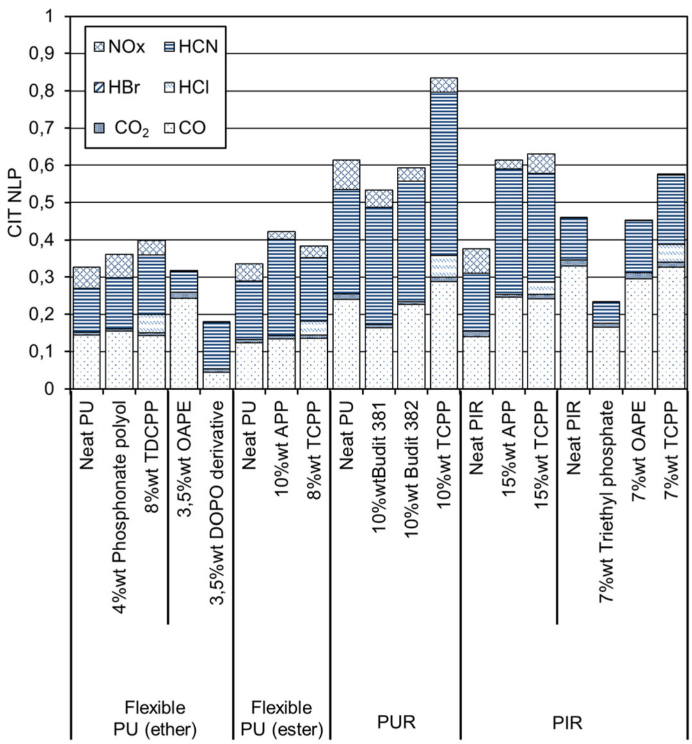

FIGURE 12 Comparison of CIT NLP values for the polyurethanes group, calculated from NF X 70-100 results.

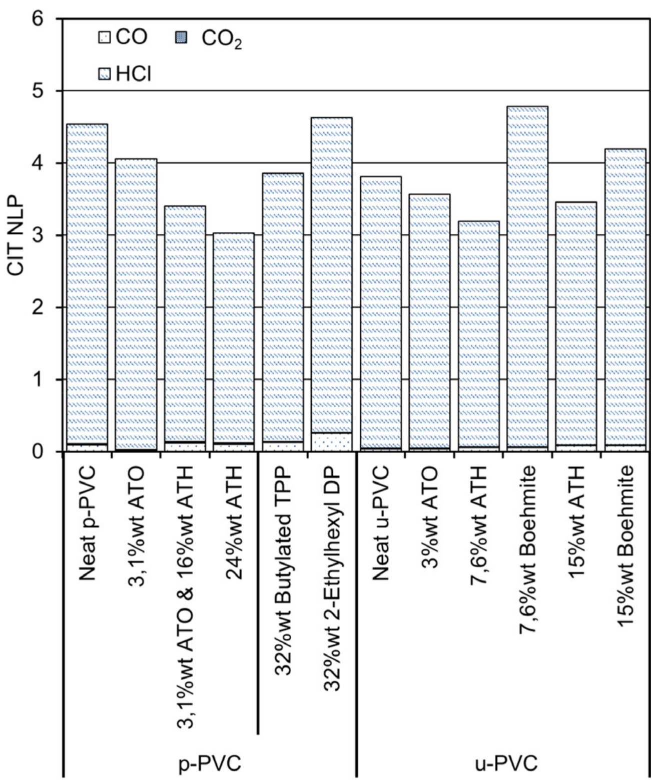

FIGURE 13 Comparison of CIT NLP values for p-PVC and u-PVC calculated from NF X 70-100 results.

flexible PU which allowed a small improvement in toxic effluents yields. For polyurethanes, fire behavior and toxicity seem to depend in part on the nature of the foam and the flame retardant, as the same FR may give different results depending on the matrix considered.

Due to its composition, PVC emits very high amounts of HCl during combustion (Figure 13) regardless of the FR used (between 218 and 353 mg g^{-1} of HCl). However, both ATO and ATH were found to slightly reduce HCl yields, although its concentration still lies at unhealthy levels. On the other hand, boehmite did not reduce HCl gas emissions in PVC. The addition of 32%wt 2-ethylhexyl diphenylphosphonate yielded worse results than 32%wt butylated triphenylphosphonate in p-PVC, with higher CO yields. Overall, the flame retardants used in PVC have only shown a minor effect on an already very high toxicity emitted by this kind of polymer.

4 | DISCUSSION

4.1 | Polyolefins

Polyolefins are not self-extinguishing materials, they present a high flammability, high heat release and generally show little smoke when they burn in air, since they are purely built on aliphatic structural units. FR-containing polyolefins are mainly used in electronic, automotive, building and seating applications. In the railway sector, they might be used in terminal strips, electronic items or small non-listed items. Smoke density is therefore usually measured at 25 kW m^{-2} rather than 50 kW m^{-2} according to R22 or R23 from EN 45545-2. Under the test conditions used here, polyolefins will therefore tend to have very fast combustion kinetics. When looking at the general behavior of these polymers, polypropylene (PP) is known to have a slow burn rate and produces very little soot and no char. High-density polyethylene (HDPE) can on the other hand produce dense smoke when burning at high temperatures. Results on neat HDPE, LLDPE and PP highlight medium smoke production at 50 kW m^{-2} (Ds_{MAX} values between 317 and 483) after a short time interval (between 3 and 5 min). These results are slightly lower than those obtained on neat 6 mm HDPE tested at 25 kW m^{-2} under non-flaming conditions (reported Ds_{MAX} value of 699).[27] The measured toxicants concentrations in the smoke chamber at 4 and 8 min indicate that the main hazards for polyolefins are CO followed by CO_2 in order of importance. One of the main challenges for FRs used in polyolefins is therefore to mitigate the emissions of CO, CO_2 as well as the amounts of smoke.

HDPE and PP samples containing DBDPE and ATO FRs reached the highest Ds_{MAX} values among tested polyolefins in the smoke chamber test. It should also be noted that the highest values of smoke toxicity (CIT_{NLP}, $CIT_{4\ min}$, $CIT_{8\ min}$) were found for this FR combination. Brominated flame retardants are known to be active in the gas phase through a radical reaction, at the expense of normal oxidation from fire. This usually leads to the formation of larger amounts of smoke at higher combustion temperatures and is already documented for LDPE treated with decabromodiphenylether and ATO.[28] Our results further highlight that this combination is detrimental to smoke production and toxicity occurring from polyolefins combustion, although useful to pass small-scale LOI, glow-wire or vertical UL94 tests which are applied to electronic products under EN 45545-2 standard (requirements R24, R25, R26 from EN 45545-2, respectively).

N-Alkoxy amine and hindered amines are mostly used as light stabilizers in polyolefins and several studies highlight that they improve fire retardancy in conjunction with APP, or even alone[29–32] N-Alkoxy amine works by quenching free radicals during combustion. In our case, the use of N-alkoxy amines or hindered amines alone inside PP and LLDPE yielded however no major improvement on smoke production at 50 kW m^{-2}. Furthermore, both compounds added NOx effluents detected by FTIR in the smoke chamber as well as in the tubular furnace method. These results could be attributed to the gas-phase action of N-alkoxy amine-FRs, which also increases smoke production. It is also possible that their flame-retardant effect is less apparent under severe heat stress (50 kW m^{-2}) due to faster combustion kinetics and quick radical depletion. According to these results, amine based FRs alone do not produce any benefit in terms of smoke emission in PP or LLDPE under these conditions.

Among the different FRs tested in polyolefins, only resins containing intumescent FRs showed a significant reduction in smoke production. Both ammonium polyphosphate (APP) in PP or piperazine pyrophosphate coupled with phosphates and zinc oxide in HDPE yielded the lowest Ds_{MAX} values (273 and 154 for two different grades of APP in PP and 427 for piperazine in HDPE, respectively), as well as a longer times to peak smoke densities. These results can be ascribed to the formation of a protective intumescent layer that reduces oxygen supply and heat exchange. The use of N-based FRs is however slightly detrimental to the toxicity evaluation, as evidenced by the tubular furnace test at 600°C. In fact, two additional noxious gases (namely, HCN and NO_X) were detected in both test methods. It should however be noted that intumescence might not take place under the static furnace conditions. Intumescent FRs therefore show no clear benefit on toxicity deriving from polyolefins degradation but yield lower smoke production at 50 kW m^{-2} in the smoke chamber test.

Polyolefin's reaction to fire is mainly dependent on the FR additive used. One of the main hazards from burning polyolefins is CO and CO_2 emissions and is produced by each sample under NF X 70-100 or ISO 5659-2 conditions, regardless of the presence of FRs. However, samples containing N-based FRs showed slight additional NO_x and HCN emissions, whereas samples containing Br-FR led to HBr formation or increased CO emissions. Radical quenchers (N-alkoxy or hindered amines, DBDPE with ATO) were not found to reduce smoke yields from polyolefins. Our results suggest therefore that, in terms of smoke emission, intumescent FRs should be preferred in polyolefins and that brominated-FRs as well as other gas-phase reaction quenchers should be avoided if smoke ought to be reduced. Hydroxide FRs could also be preferred to Br-FR in polyolefins since they have been shown to reduce smoke production alone or in conjunction with synergists.[33,34] Reduction of smoke toxicity in polyolefins might nevertheless prove to be more difficult to achieve through incorporation of FRs.

4.2 | Epoxy composites

Composites based on epoxy resins and glass fibers are usually found in electronics, industrial equipment, mass transportation and building applications. In the railway sector, they are typically used for partitions, floors and large indoor or outdoor surfaces (R1 and R7 from EN 45545-2) and covered with paint and gelcoat. Some of these coatings are used to improve the fire properties of resins that have a poor reaction to fire. In fact, epoxy resins present high mechanical, chemical and heat resistance but lack fire resistance and produce high levels of smoke during fires. In this study, neat epoxy resins tested without any varnishes or paints showed very high levels of smoke density (Ds > 792 after 140 s). Strategies adopted to reduce fire-toxicity and smoke include for example the addition of zinc-based FR, functionalized graphene or modification of glass fibres.[35–37] Epoxy resins loaded with aluminium methylethylphosphinate or aluminium diethylphosphinate can attain for example UL94-V0 classification, as well as LOI values above 29%.[38] Low loading levels of molybdenum disulfide nanosheets grown on titanate nanotubes were also found to reduce smoke emissions from epoxy samples at 50 kW m^{-2} in the ISO 5659-2 smoke chamber test.[24]

Our results indicate that samples containing tetrabromobisphenol-A (TBBPA) or aluminium diethylphosphinate (AlPi) show no significant improvement in smoke production under the smoke chamber conditions at 50 kW m^{-2}. Only ammonium polyphosphate (APP) significantly decreases smoke density in all epoxy samples (regardless of their thickness) and is accompanied by a reduction in mass loss. The smoke reducing effect of APP in epoxy is slightly more pronounced than the inclusion of 3%wt molybdenum disulfide nanosheets grown on titanate nanotubes (Ds_{MAX} of 451, tested at 3 mm and 50 kW m^{-2}).[24] Intumescent-FRs are known to create a barrier which starves the flame and reduces the rate of pyrolysis and have already been documented to be efficient in reducing smoke production from epoxy resins.[39] Our results therefore confirm this trend and indicate that these FRs are adequate to reduce the amount of smoke emitted by epoxy resins.

Toxicity from epoxy mainly comes from CO and CO_2 during thermal degradation, with small amounts of NO_x and HCN depending on the nature of the resin, additives, as well as the fibres used inside the material. Our results indicate that APP with N-based synergists increase HCN and NO_X production from epoxy samples by a small amount but reduce CO yields (Figure 10). The Br-FR based sample shows significant HBr emissions which dramatically increases the overall toxicity of the gaseous mixture in the NF X 70-100 test method (CIT_{NLP} value of 0.44 vs. 0.18 for neat epoxy sample). This is attributed to the nature of the FR used and its gas-phase mechanism. The different FRs tested in epoxy resins therefore show only a very limited impact on smoke toxicity. Our results further highlight that the use of intumescent FRs in epoxy resins appears to be the best compromise to reduce smoke, as well as CO and CO_2 production. However, HCN and NO_x amounts should be systematically monitored to ensure that the introduced FRs do not show an adverse effect on toxicity.

4.3 | Polycarbonate

Polycarbonate has an intrinsic flame-retardant property, due to its high thermal stability and its tendency to produce char when burning. Its high-impact resistance combined with good electrical insulating properties make it an ideal candidate for electrical, electronic and automotive applications. Due to its properties and transparency, it can be found as a light diffuser (R4 from EN 45545-2, typically tested at 50 kW m^{-2} under ISO 5659-2), windows or E&E material in rolling stock. However, polycarbonate produces high amounts of smoke and carbon monoxide when burning, due to its aromatic backbone.[3] Smoke chamber tests performed on neat PC showed a rapid evolution of smoke after a short time (Ds > 792 after 190 s). Inclusion of Br-FR such as brominated bisphenol-A in PC yielded no improvement of smoke production or smoke toxicity. Inclusion of 20%wt P-based FR in PC also displayed limited impact. In fact, carbon monoxide emissions and conventional indexes of toxicity (Figure 9, CIT_{NLP}) remain in the same range for all tested PC samples, regardless of their composition. The impact of the FRs examined within this study on PC smoke emission is therefore limited. However, various innovative solutions have been developed for this resin and satisfactory results can be achieved through the incorporation of nanofillers or macrocyclic polyphenylsilsesquioxanes compounds.[40,41]

4.4 | Polyamides

Due to their suitable combination of thermal, dielectric and mechanical properties, polyamides are widely used in many industrial fields, such as electrical and electronic applications, synthetic fibers, textiles, automotive engineering and home furnishing. In the scope of railway applications, polyamides might find applications in plastic casings or E&E components. Polyamides present a high flammability, heat and smoke production. The thermal degradation of polyamides is well reviewed in the literature and the formation mechanism of several hazardous combustion products has been well established.[16,26] PA6 and PA66 have very different decomposition products: PA6 mainly produces cyclic oligomers and monomers, whereas PA66 breaks into fragments of adipic acid and other secondary products. Polyamides typically generate HCN, NOx, CO, CO_2 and H_2O when burning, with increasing HCN and CO yields along with temperature growth. Among these toxicants, HCN and CO are the main hazards in polyamide combustion. Smoke suppression can be for example accomplished through the incorporation of aluminium hydroxymethylphosphinate (AHMP) and melamine pyrophosphate (MPyP) or oligomeric aryl phosphates.[42,43]

Under the same testing conditions and at the same thickness, neat PA6 was found to emit less smoke (Ds_{MAX} values varies between 188 and 424) than PA66 (Ds_{MAX} between 511 and 616). Magnesium hydroxide shows a drastic reduction of smoke in PA 6 (Ds_{MAX} of 92 at $t = 136$ s) when compared to its non-FR counterpart (Ds_{MAX} of 424 at $t = 308$ s). Furthermore, toxicity measurements carried out by FTIR in the smoke chamber test show a comparable level of toxicity to the reference sample. This result is confirmed under different testing conditions by the tubular-furnace test, which yields appreciably similar levels of smoke toxicity but higher CO and CO_2 yields, and lower HCN and NO_X emissions. Magnesium hydroxide classically acts through the release of water which produces an endothermic effect and reduces the kinetics of combustion, but its mode of action in polyamide may be different and promote charring instead. Our results are comparable with those obtained with aluminium hydroxide in PA6 or PA66 carpets, which was shown to be an efficient smoke reducing FR under both flaming or non-flaming conditions of the ASTM E662 smoke chamber test method.[12]

Melamine cyanurate is mainly used alone in polyamides as an agent promoting non-flaming drips and extinction by dilution of oxygen and fuel gases. It yields excellent results in small-scale flammability tests (e.g., LOI, UL94, glow wire). But the smoke reducing effect of melamine cyanurate is usually only observed in conjunction with synergists, such as MoS_2[44] or magnesium hydroxide.[45] Our results indicate that the use of melamine cyanurate alone increases the amounts of smoke generated by PA6 as well as PA 66 in the ISO 5659-2 smoke chamber test at 50 kW m^{-2} (Figure 5). Our results also indicate that MC increases HCN and NO_x yields in PA6 while decreasing CO and CO_2 emissions. In PA66, MC acts differently: higher CO, CO_2, and

NO_x emissions were found and HCN yields decreased. These results are consistent with the literature, which indicates that MC has different degradation mechanisms in PA6 and PA66.[26] Our results reveal that although MC can be used alone to pass small-scale flammability tests, it can negatively impact smoke emissions and toxicity in a fire.

Melamine polyphosphate (MPP) acts through a condensed-phase mechanism and promotes char formation in polyamides. In PA66, MPP produced diverging results under the smoke chamber test conditions, either slightly increasing smoke production or reducing it when considering different PA66 grades. Interestingly, the presence of MPP in PA66 causes either a decrease in the yields of toxicants (in the case of Budit 610 and 342) or a slight increase. These results might be ascribed to the different grades of MPP (different morphologies and granularities) and grades of PA66 (molecular weight, viscosity and charring capacity) provided.

Our results highlight that reducing smoke emissions in PA6 and PA66 can be achieved through the incorporation of magnesium hydroxide or certain grades of intumescent FRs such as MPP. These FRs also show limited impact on smoke toxicity. Other strategies adopted to date to reduce polyamides flammability are not without risk: the use of MC or Br-FR systems in PA6 or PA66, although useful to pass small-scale flammability tests such as LOI and UL94,[46] can increase smoke production and toxicity. Such FRs in PA6 or PA66 matrixes should be avoided, or used with a synergist, when smoke or toxic effluents are an identified hazard in the envisioned fire scenario.

4.5 | Polyurethanes

Polyurethanes (PU) foams can be categorized according to cell size (nano, ultra-micron, micron or macro-sized pores) as well as morphology type: closed-cell morphology usually leads to rigid PU whereas open-cells or connected morphologies yield flexible PU. Depending on their rigid or flexible nature, polyurethanes can be used either as thermal insulating materials (rigid foams) or in sound and vibration attenuation applications as well as cushioning (flexible foams). These uses are critical in trains for passenger comfort (noise and temperature insulation, seating) but are accompanied by significant fire hazards. In fact, polyurethanes are mainly used in building insulation, bedding, furniture, yet are the most flammable part and most predominant component of upholstery. Indeed, the main fire hazards of polyurethanes are high heat release rates, high smoke production and toxicant levels. Flexible PU cushioning is highly flammable, burns rapidly, can drip, and often leaves a brown liquid residue after combustion. Rigid polyurethane can be found as an insulation item in facades or trains and be the cause of devastating fires. High density PU foams generally produce more smoke than low density PU. Due to their rich nitrogen content, polyurethanes are also expected to release high concentrations of HCN and NO_x during combustion. Polyurethane combustion is complex and depends on several factors, including the nature of the foam (rigid or flexible), structure of the polyol, isocyanurate index, FR nature and loading, porosity as well as foam density.[47] Moreover, polyurethane fire retardancy is challenging and might be accompanied by a loss of properties (discoloration of the foam, instability of FR due to humidity, loss of mechanical properties), thus making FR selection limited.

Flexible polyurethane foams show Ds_{MAX} values between 163 and 318 under the ISO 5659-2 smoke chamber test at 50 kW m^{-2} and under non-flaming conditions. Under the same testing conditions, rigid PU foams show Ds_{MAX} values between 91 and 250. These values are consistent with previous data reported earlier.[47] The toxicity data collected indicates that rigid PU yields the highest amounts of toxicants (mainly CO and HCN) at 600°C in the NF X 70-100 test method. This result may be expected considering that flexible PU is thermally less stable than rigid PU and is less prone to char formation during combustion. A recent study by Günther et al. suggested that preservation of cellular structure in PIR foams during combustion could explain their superior fire performance when compared to PUR.[48]

All P-based FRs used in flexible PU foams (oligomeric alkylphosphate ester, DOPO derivative and TDCPP) brought a small increase in smoke production. On the other hand, TCPP, APP and phosphates (triethyl phosphate or oligomeric alkyl phosphate ester) all yielded slightly lower smoke density values in rigid foams compared to their neat polymer counterparts and to flexible PU. The open cell structure of flexible foams could be at the origin of this discrepancy observed with rigid foams. We hypothesize that an open and flexible cell structure could facilitate the diffusion of oxygen and collapse of the char or the foam structure and limit FR effectiveness.

Among the different FR systems tested inside PU foams, TCPP and TDCPP both show increased smoke toxicity due to gaseous HCl release, related to their composition (chlorine-based FR). PU samples treated with oligomeric alkyl phosphate ester shows a higher CO and smaller HCN release compared to the DOPO derivative sample. APP showed variable behaviour depending on its matrix: flexible PU ester samples or PIR including APP showed slightly higher smoke toxicities than their neat polymer counterpart, in part with higher HCN emissions. Nevertheless, rigid polyurethane (PUR) shows a lower CIT_{NLP} value when treated with APP (Budit 381 or 382). Triethyl phosphate was also found to reduce smoke toxicity from polyurethanes inside the scope of this study. It is suggested that phosphorus based FRs show different modes of action depending on their thermal stability as well as their valency.[49–51] Our results point out that P-based FRs action is indeed complex and is also ascribed to the nature of PU foam: P-based FRs seem to be more efficient for smoke reduction in rigid foams than flexible ones.

4.6 | Polyvinyl chloride

Due to its high chlorine content, PVC is inherently fire-resistant and difficult to ignite. Samples of u-PVC burn with difficulty, are self-extinguishing and produce white acidic smoke whereas p-PVC can burn readily; its combustion behavior depends on the nature of the plasticizer. PVC mainly finds applications in cables, building and automotive applications where most FRs used are either inorganic or phosphorus based. In the railway sector, PVC is mainly used alone or in conjunction with other materials as floor covering, artificial leather, cable sheathing, stickers, pipes and fittings. Among the p-PVC samples tested, no FR was found to significantly decrease smoke production at 50 kW m^{-2}. However, boehmite was found to have a very positive impact on smoke yields in u-PVC, which is surprising and not documented to our knowledge. Boehmite is generally regarded as being of intermediate effectiveness in terms of reaction to fire, between aluminium trihydroxide and aluminium oxide.

PVC samples show a high toxicity regardless of their FR content, with CIT_{NLP} values between 3.0 and 4.6 for p-PVC and between 3.2 and 4.8 for u-PVC. This toxicity is mainly ascribed to the high chlorine content of the polymer and its release in gaseous form during thermal degradation. It is therefore extremely difficult to reduce the gaseous emissions of this family of polymers. In the scope of this study and under the tested conditions presented here, flame retardants have only a minor impact on the toxicity measured from burning PVC. Both antimony trioxide (ATO) and aluminium hydroxide (ATH) show limited effectiveness to reduce the amount of HCl released by u-PVC and p-PVC. Boehmite, although efficient at reducing smoke production in the ISO 5659-2 smoke chamber test, increases HCl production in the NF X 70-100 test with CIT_{NLP} values (4.2 and 4.8) above neat u-PVC (3.8). This effect is more pronounced at a lower FR loading. Butylated triphenyl phosphate (BTPP) has a better effect on HCl reduction than 2-ethylhexyl diphenyl phosphate (EHDP). Overall, flame retardants have only a limited impact on the high toxicity and smoke emitted by PVC.

5 | CONCLUSION

The aim of this study was to evaluate the influence of commonly used flame retardants added to different types of polymers on smoke density and toxicity and answer the question "do flame retardants lead to more smoke formation from burning polymers and do they make it more toxic?" The combustion products were evaluated according to two different methods of analysis and scenarios. The French tubular furnace method (NF X 70-100) at 600°C is used inside the EN 45545-2 for small items. The European smoke chamber method at 50 kW m^{-2} and without pilot flame (ISO 5659-2) equipped with a FTIR analyzer (EN 45545-2, Annex C) generally represents post-flashover conditions and is used for products with large surface areas. This study sheds some light on the fire behavior of FR polymers and general trends for certain classes of FRs. We emphasize here that the results were obtained on a limited number of samples and under restricted conditions. Such results account for the behavior of materials subject to specific fire test conditions; they do not purport to represent the only criterion for assessing the potential fire hazard posed by the product under the conditions of use. Furthermore, the obtained results may vary deeply depending on polymer nature, thickness, color, density, and additives. In most cases, halogenated FRs were found to be detrimental to smoke production as well as toxicity evaluation when compared to neat polymers due to their mode of action and their chemical composition. In contrast, even a reduction of smoke formation can often be achieved in the ISO 5659-2 test through the incorporation of intumescent or other adequate non-halogenated FRs, whereas the impact on toxicity (when measured through NF X 70-100 or Annexe C from EN 45545-2+A1:2016) is limited. In a few cases, PIN FRs have been found to reduce the toxicity of smoke in this study, whereas in others, it is moderately increased.

PC and PVC are both intrinsically fire-resistant and hardly show any diminution in smoke or toxicity measured at 50 kW/m^2 in ISO 5659-2 and NF X 70-100 at 600°C when Br-FRs or phosphorus-based FRs were added. However, boehmite was found to drastically reduce smoke production in u-PCV and further work should be done in the NBS smoke chamber test to elucidate its mode of action.

Polyolefins and epoxy samples with FRs emit effluents related to their chemical composition when burning. Nitrogen-based FRs increase the HCN and NOx levels in NF X 70-100 and Annexe C from EN 45545-2+A1:2016 tests, albeit in small proportions. In this regard, N-alkoxy amines and hindered amines used alone bring no benefit to smoke and toxicity issues, but intumescent FRs such as APP were found to be efficient in reducing smoke production in the NBS smoke chamber test at 50 kW/m^2. Such an approach should be preferred to limit the impact of FRs on smoke and toxicity and might be combined with synergists to reduce flammability.

Polyamides demonstrate variable behavior when testing them following EN 45545-2+A1:2016 standard, depending on their composition and the nature of the FR employed. Melamine cyanurate, one of the most widely used and widespread FR compounds in polyamides, was found to be slightly detrimental to smoke toxicity and increase smoke production when used alone in polyamides, especially in PA6. We therefore suggest that MC should preferably be used in conjunction with other FRs and synergists to limit these adverse effects. Other FRs such as magnesium hydroxide or MPP could reduce smoke in polyamides without significantly affecting its toxicity and could therefore be preferred to MC in terms of smoke emissions. The phosphorus-based FR and MPP, both tested in PA66, had a neutral effect and should be preferred to Br-FRs in polyamides.

PIN FRs used to reduce flame propagation or ignitability in polyurethanes influence smoke and toxicity to a lesser degree in NF X 70-100 and ISO 5659-2 tests. Phosphorus-based FRs in PUs have little impact on smoke production and their effectiveness depends on the nature of the foam (rigid or flexible). In this regard, rigid PU generally shows better behavior than flexible PU, although both types of foam have comparable smoke toxicities. However, these two types of foams do not find the same applications and cannot be interchanged. The fireproofing strategy must therefore be adapted on a case-by-case basis.

Our results underline that the choice of a FR is significant and implies to consider the different aspects of polymer reaction to fire as well as the envisioned fire scenario and its hazards: ignitability, flame spread rate, toxicity, smoke production and heat release. In addition to these considerations, one also must consider issues of cost, processability, chemical, mechanical, aesthetic properties as well as recyclability and environmental impact. The use of FRs to pass a single fire test or to meet a single requirement addresses only one parameter from the most-likely fire scenario. Other aspects such as toxicity or smoke are generally not studied further. Fire testing is resource-consuming and fire scenarios are varied and difficult to predict, but small-scale tests can be useful for comparative evaluation of FR fire-performance. The design of fire-safe materials is challenging since it must reduce most fire-related risks with a limited impact on toxicity and smoke. The present study may help to choose adequate fire-retarding strategies to apply for products used in the European railway market and EN 45545-2+A1: 2016. The most efficient FRs should therefore be designed and chosen with the appropriate matrix to meet an optimum, where their benefits exceed their disadvantages. Nevertheless, the conclusions of this study are not exhaustive. Other fire scenarios have not been evaluated and additional tests in the NBS smoke chamber at 25 kW/m^2 (with and/or without pilot flame) or NF X 70-100 tests at 400°C and 800°C could be undertaken in order to consolidate these results and the conclusions obtained.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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