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Flame retardant surface treatments for rigid polyurethane foams used in the building sector: Current state-of-the-art and perspectives

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ABSTRACT

Rigid polyurethane foams are widely employed in the building sector, mainly as thermal insulating materials. On the one hand, they can easily be sprayed or applied as rigid insulation panels, providing exceptional thermal resistance, lowering heat transfer, and contributing to building energy efficiency. However, polyurethane foams are easily flammable when exposed to a direct flame or an irradiative heat flow. This drawback significantly limits their exploitation, especially when flame retardancy is an undeniable prerequisite. Notwithstanding the possibility of providing flame retardant features to polyurethane foams through either the incorporation of effective flame retardant additives into the foam formulation or the chemical modification of the monomers (i.e., the diols or polyols) with flame retardant species (usually containing P and/or N elements) before the synthesis of the polyurethane, one of the current strategies relies on the use of flame retardant surface treatments directly applied to the foamed materials. Indeed, the flammability of polyurethane foams is a surface-localized phenomenon that can be quite effortlessly and effectively controlled by tailoring their surface through the deposition of efficient flame retarded treatments (e.g., layer-by-layer architectures, coatings (also UV-curable), and "one-pot" deposited complexes/colloids). This work is aimed at reviewing the latest research outcomes about the use of effective surface treatments for rigid polyurethane foams, providing the reader with the current limits and some perspectives for the forthcoming years.

1. Introduction

Polyurethanes (PURs) are polymers derived by reacting either aliphatic or aromatic diisocyanates with diols/polyols [1]. They exhibit a wide range of physico-chemical properties that make them versatile materials for various application sectors, including civil engineering [2–5], the biomedical field [6,7], and the transportation sector [8,9], among others. The global market size of rigid polyurethane foams was estimated at USD 20.69 billion in 2023; it is expected to grow at a CAGR of 5.8 % from 2024 to 2030 [10].

Specifically referring to the construction sector, PURs are currently employed for thermal insulation purposes (i.e., as insulation materials for floors, roofs, and walls) [11–14], as sealants and adhesives (to seal joints, fissures, and cracks in floors, walls, doors, and windows) [15,16], as protective/waterproof coatings [17,18], and as structural components (in lightweight glass- or carbon fiber-reinforced composites to be used as beams, pillars, panels, and roofing elements) [19,20].

Apart from their uses as bulk materials, PURs are well-known and exploited as foamed materials. The history of polyurethane foams dates to 1937, when Otto Bayer unveiled the suitability of polyaddition reactions for their synthesis [21,22]. Conversely, the fast industrial development of PURs took place only in the 1960s, with the invention of the foaming manufacturing equipment [23].

Generally speaking, polyurethane foams are classified into three groups: flexible, semi-rigid, and rigid. The first two foams are mostly employed in the upholstery industry, while flexible foams are also utilized as sound-insulating materials. In contrast, rigid polyurethane foams are predominantly used as materials for thermal insulation: these features strictly depend on the internal structure and, in particular, on the microstructure and morphology of the foam cells [24].

The interesting thermal and mechanical properties of rigid polyurethane foams are somehow limited by the materials' high flammability when exposed to an irradiative heat flux or a direct flame, also because of the peculiar low-density porous structure that speeds up the combustion rate [25–30]; besides, their combustion may account for the emission of toxic smoke containing NO_x, CO, and HCN, which are

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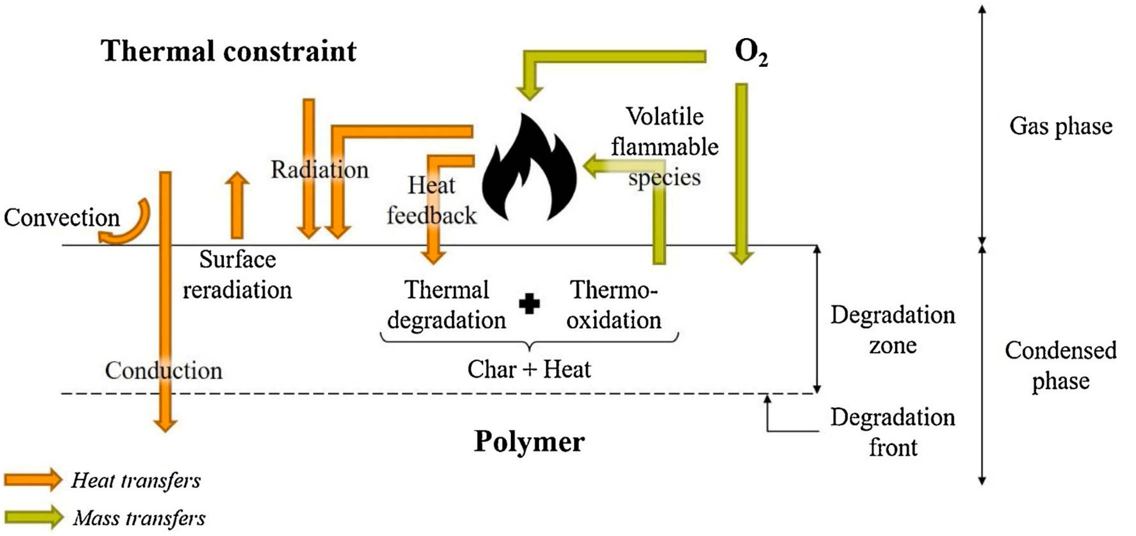

Fig. 1. Polymer combustion cycle. Reprinted with permission from [56]. Copyright Elsevier, 2021.

harmful to humans and animals [31–34].

All the abovementioned issues highlight that it is now very demanding to make rigid polyurethane foams resistant to fire [35,36]. This is a key target: indeed, statistics from 2021 and 2022 showed that more than 6000 people died, and billions of USD worth of property was destroyed by high-rise building fires [37].

The currently exploited strategies for conferring flame retardant properties to rigid PURs involve reactive methods, additive techniques, and surface treatments [38–44].

Reactive strategies adopt the incorporation of reactive flame retardant additives (usually based on Phosphorus, Boron, Nitrogen, Silicon, and Sulfur) directly into the polyurethane matrix, exploiting the chemical reactivity of the additives themselves [45–47]. However, despite a generally very effective flame retardant behavior imparted by these additives, their main drawback relies on the worsening of the thermal insulation characteristics of the foamed flame retarded PURs, because of the usual lowering of the efficiency of the foaming process [48,49]. Similarly, the use of additive strategies is usually limited by the need to incorporate high loadings of non-reactive flame retardants in the polymer matrix, hence negatively impacting the foaming process [50–52]. Besides, it is possible to employ bio-sourced flame retardant additives [53,54], hence fulfilling the current and demanding circular economy concept [55]. All these limitations can be successfully overcome by using effective surface treatments directly performed on the already foamed material. This way, the inherent features of the latter are not affected, and the foams may show outstanding flame retardant performance. This strategy undoubtedly exhibits great potential as it concentrates the fire retardant effect at the interface between the foamed material and the surrounding environment, i.e., where it is a prerequisite. Besides, a lower quantity of flame retarded coating is employed, and there are no compatibility issues with the underlying polyurethane matrix [56,57].

Regardless of the type of adopted flame retardant strategy, providing polymers with flame retardancy means being able to effectively interfere with their combustion process. From an overall perspective, the latter involves a multifaceted and self-sustaining mechanism, encompassing reactions that might take place in the condensed and/or gas phases (Fig. 1). Besides, heat and mass transfer occurring at the interface between the polymer and the flame are the key phenomena responsible for the whole fire behavior. Upon heating at elevated temperatures, the polymer undergoes thermal decomposition that may involve thermo-oxidative reactions in the presence of air (oxygen). Thermal and thermo-oxidative phenomena also lead to the formation of low

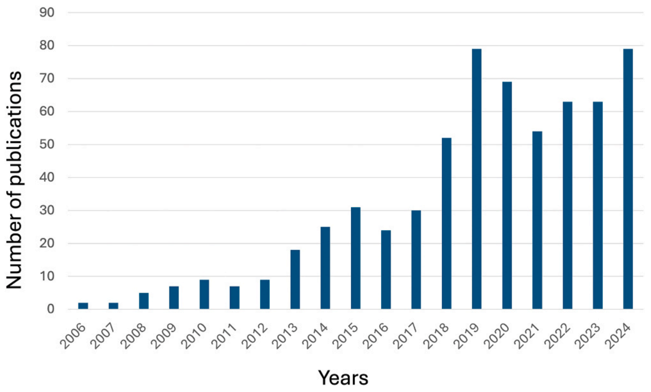

Fig. 2. Number of publications (from 2006 to 2024) in peer-reviewed journals, dealing with “rigid polyurethane foams AND flame retardant” (where AND is the Boolean operator; data collected from the Web of Science™ database, accessed on Jan 2, 2025).

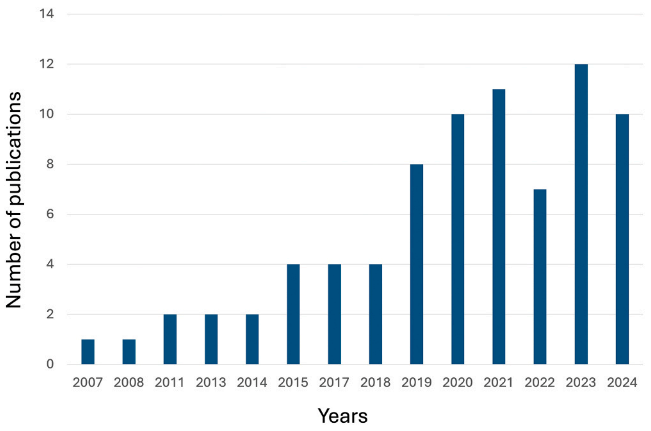

Fig. 3. Number of publications (from 2007 to 2024) in peer-reviewed journals, dealing with “rigid polyurethane foams AND flame retardant AND coating” (where AND is the Boolean operator; data collected from the Web of Science™ database, accessed on Jan 2, 2025).

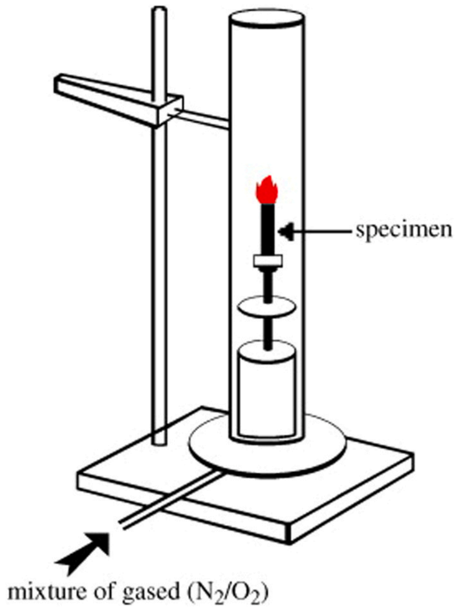

Fig. 4. Scheme of the LOI apparatus. Reprinted with permission from [61]. Copyright Elsevier, 2009.

molecular weight volatile molecules and radical species. After their release into the gas phase, the volatile molecules and the formed $OH^{\cdot}$ and $H^{\cdot}$ radicals give rise to the formation of a combustible mixture with air, which burns if the temperature is sufficiently high (i.e., beyond the so-called ignition temperature) or in front of an external energy source (e.g., an electric arc, or a spark). The combustion reactions that ensue are responsible for the production of light, the emission spectrum of which is closely linked to the constituent species within the flame. These reactions are characterized by a pronounced exothermic nature. A part of the evolved heat is directed back to the polymer and helps sustain its combustion reactions until flammable mass or oxygen is depleted. In addition, some of the non-volatile species originating from thermal or thermo-oxidative decomposition reactions can significantly contribute to limiting the quantity of flammable products, mainly through the formation of a protective carbonaceous layer (i.e., the so-called *char*).

The academic interest in conferring flame retardant properties to PURs is well documented by the continuously increasing number of publications that have appeared so far in the scientific literature (Fig. 2); this is still true if one narrows the search to surface treatments only (Fig. 3).

This work aims to summarize the latest research outcomes dealing with the use of efficient flame retardant treatments derived from layer-by-layer architectures, coatings, or “one-pot” deposited complexes/colloids onto rigid polyurethane foams, providing the reader with several up-to-date “case studies”. Besides, the current limits of the proposed flame retardant surface treatments will be discussed, and some perspectives for their future development and implementation will be envisaged.

2. How to assess the fire behavior of rigid polyurethane foams from a lab-scale perspective

This paragraph briefly summarizes the main tests that can be carried out to assess the fire behavior of rigid polyurethanes to meet the expectations of readers unfamiliar with these kinds of measurements. For a more in-depth reading, it is suggested to refer to some of the nice papers published in the scientific literature [58–60].

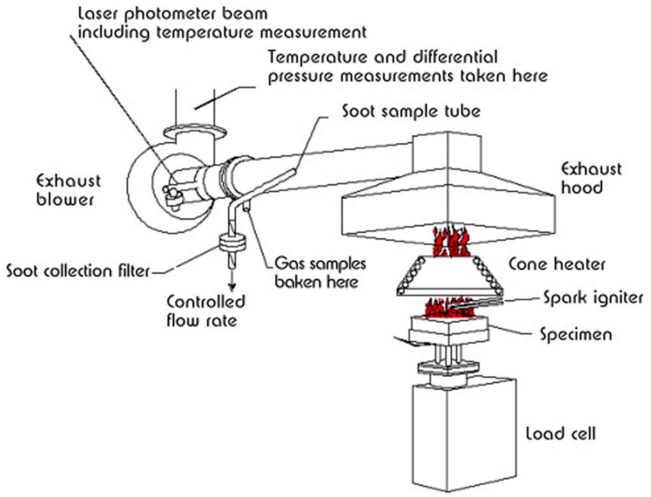

Fig. 5. Scheme of the cone calorimeter. Reprinted with permission from [61]. Copyright Elsevier, 2009.

Ignitability, flame spread rate, and heat release are the three main parameters for assessing the fire behavior of rigid polyurethane samples. Specifically referring to lab-scale tests, the most usual tests include the Limiting Oxygen Index (LOI), UL94 vertical flame spread, and cone calorimetry tests: the first two are flammability measurements, while the last is classified as a forced-combustion test.

2.1. Limiting oxygen index (LOI) measurements

LOI (Fig. 4) determines the minimum vol% of O_2 in a flowing O_2/N_2 mixture to maintain the combustion process of a sample [61]. The LOI value is calculated according to Eq. (1):

$$LOI(\%) = \frac{O_2}{O_2 + \quad N_2}100 \tag{1}$$

The specimen is vertically positioned in the middle of a glass chimney, following the ASTM D2863 standard. The O_2/N_2 mixture is flowed upward through the glass chimney for 30 s to reach a homogenous burning atmosphere. After the ignition at the top, the specimen starts burning downwards in a candle-like manner. Then, the O_2 concentration in the O_2/N_2 mixture is decreased until a critical concentration is achieved. As the standard O_2 vol% is approximately 21 %, all specimens exhibiting an LOI value above this are classified as self-extinguishing in atmospheric conditions following the removal of the external flame source. Conversely, polymers showing an LOI value below 21 % are designated as self-combustible.

2.2. Cone calorimetry tests

The cone calorimeter (Fig. 5), developed at the National Bureau of Standards (NBS, at present the National Institute of Standards and Technology, NIST) in the early 1980s [62], is the most universally employed bench-scale heat release rate apparatus [63]. Following the ISO 5660 standard, a square sample (generally 100 × 100 × 4 mm^3 sized) is exposed to a constant irradiative heat flux (from 10 to 100 kW/m^2) provided by a conical electric heater. The ignition of the pyrolysis products released by the specimen is accomplished utilizing an electric spark: in particular, Time-to-ignition (TTI, s) is a critical fire reaction property as it defines how rapidly flaming combustion of the sample will occur when exposed to the irradiative heat source of the conical heater. The electric spark igniter is then withdrawn as soon as sustained flaming is observed. An exhaust hood captures the gases that originate during the combustion of the specimen; then, these gases are analyzed as far as their temperature, pressure, flow rates, relative compositions in terms of CO, CO_2, and O_2, and smoke density are considered. By measuring the oxygen depletion and the mass flow rate in the exhaust duct, it is possible to calculate the heat release rate per unit

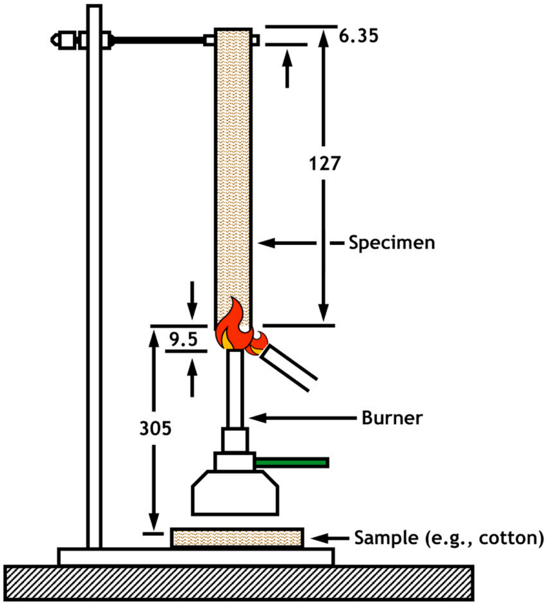

Fig. 6. Scheme of the experimental setup for UL94 vertical flame spread tests. The dimension units are in mm. Reprinted with permission from [67]. Copyright Elsevier, 2023.

of surface area (HRR, kW/m^2) and its changes over time. Among the thermal parameters monitored during the test, the peak of heat release rate (pHRR, kW/m^2), which corresponds to the maximum heat release rate measured during combustion, and the total heat release (THR, MJ/m^2), which is calculated by integrating the HRR vs. time plot, provide an overall picture of the fire behavior of the tested polymer system. Then, it is possible to measure the effective heat of combustion (EHC, MJ/kg), which represents the ratio of heat release rate to mass loss rate, averaged over the test duration or the entire test when ignition does not occur, as well as the average specimen mass loss rate per unit area (MLR, g/m^2·s), calculated over the test duration. Further, such smoke parameters as smoke extinction area (SEA, m^2/g), total smoke production (TSP, m^2), and smoke production rate (SPR, m^2/s) are evaluated [64]. Usually, the incorporation/modification of polymer systems with effective flame retardants accounts for a significant decrease in both pHRR and THR values, compared to the unmodified counterparts.

Quite recently, Vahabi and co-workers [65,66] proposed a novel universal dimensionless index called Flame Retardancy Index (FRI): it is defined as shown in Eq. (2) and allows for classifying flame-retarded polymeric materials by simply combining pHRR, THR, and TTI gathered from cone calorimetry data. More specifically, using a logarithmic scale, the flame retardancy performance of a polymer composite compared with the neat counterpart (i.e., the reference), is categorized on a logarithmic scale as Poor (FRI < 10^0), Good ($10^0 \leq$ FRI < 10^1), or Excellent (FRI $\geq 10^1$).

$$FRI = \frac{\left[\left(\frac{pHRR}{TTI}\right) \times THR\right]_{Neat\ Polymer}}{\left[\left(\frac{pHRR}{TTI}\right) \times THR\right]_{Flame\ retarded\ Polymer}} \tag{2}$$

2.3. UL94 vertical flame spread tests

Developed by Underwriters Laboratory Inc., these tests aim to evaluate the ignitability and flame spread rate of vertically oriented polymeric systems [61]. The standard experimental setup for UL94 vertical flame spread tests is schematized in Fig. 6. Following the UL94 standard (ASTM D3801), the sample (127 × 13 mm^2) is to be clamped in a vertical position, placing some cotton indicator 300 ± 5 mm below the sample itself. Subsequently, a 20 mm blue flame (gas: methane) is applied 10 mm from the bottom of the sample for 10 s and then removed; the after-flame time (i.e., the time during which the sample keeps on burning even after the removal of the external flame source) is recorded. Subsequently, the flame is reapplied to the sample immediately following the extinction of the flame for 10 seconds. The after-flame time and after-glow time (i.e., the time during which the sample continues to glow after the termination of flaming or after the removal of external methane flame) are then recorded, with observations made of the dripping phenomena of incandescent sample drops and their possible ignition of the cotton indicator. At least five samples for each polymeric system are tested to get more reproducible and accurate data. Finally, the polymeric system is categorized into V0-V1-V2 or NC (not classifiable) ranking (*see* Table 1). In this classification, V0 represents the highest rank and is, thus, referred to as a self-extinguishing polymer system.

Table 1
UL94 vertical flame spread tests – classification (any material that does not fit any of the criteria listed in the table is not classifiable - NC).

	Ranking		
Criterium	V0	V1	V2
After-flame time after the application of the first flame (s)	≤ 10	≤ 30	≤ 30
After-flame time + after-glow time after the application of the second flame (s)	≤ 30	≤ 60	≤ 60
Total after-flame time for all the five samples after the application of both first and second flame (s)	≤ 50	≤ 250	≤ 250
Flame or glow up to the sample clamp	no	no	no
Dripping phenomena or ignition of the cotton indicator	no	no	no

3. Rigid polyurethane foams: analysis of the smoke

It is well known that polyurethane foams produce large amounts of smoke during combustion; however, most of the smoke is produced in the initial stages of combustion, as assessed by Herrington [68]. In addition, there does not appear to be a significant difference in the typical smoke produced by the pyrolysis and combustion of flexible or rigid polyurethane foams [69].

Wolley and co-workers [70] investigated the combustion of rigid polyurethane foams carried out in a silica tube placed in a furnace and heated up to 1000°C in air atmosphere. The combustion products primarily detected were nitrogen-containing compounds (such as benzonitrile, pyridine, methyl pyridine, acetonitrile, acrylonitrile, propionitrile, and HCN), hydrocarbons (butadiene, toluene, propane, ethylene, and ethane), and oxygen-containing compounds (specifically identified as carbon monoxide, carbon dioxide, and water).

Blomqvist and co-workers [71] investigated the composition of the smoke originated from the combustion of rigid polyurethane foams by Fourier transform infrared spectroscopy. To this aim, the samples were irradiated under a cone calorimeter at 35 kW/m^2 irradiative heat flux: high concentrations of amines, amino-isocyanates, and isocyanates were observed.

These products were recently confirmed and quantified by Reinerte and co-workers through evolved gas analysis, a method that combines thermogravimetric/differential thermal analysis-Fourier-transform infrared spectroscopy (TG/DTA-FTIR) and pyrolysis gas chromatography-mass spectrometry (Py-GCMS) [72].

4. Surface treatments for rigid polyurethane foams: involved flame retardant mechanisms

This paragraph will detail the general mechanisms through which flame retardancy occurs in surface-treated rigid polyurethane foams. Indeed, the development of effective surface-engineered flame retarded systems relies on fully understanding the involved combustion

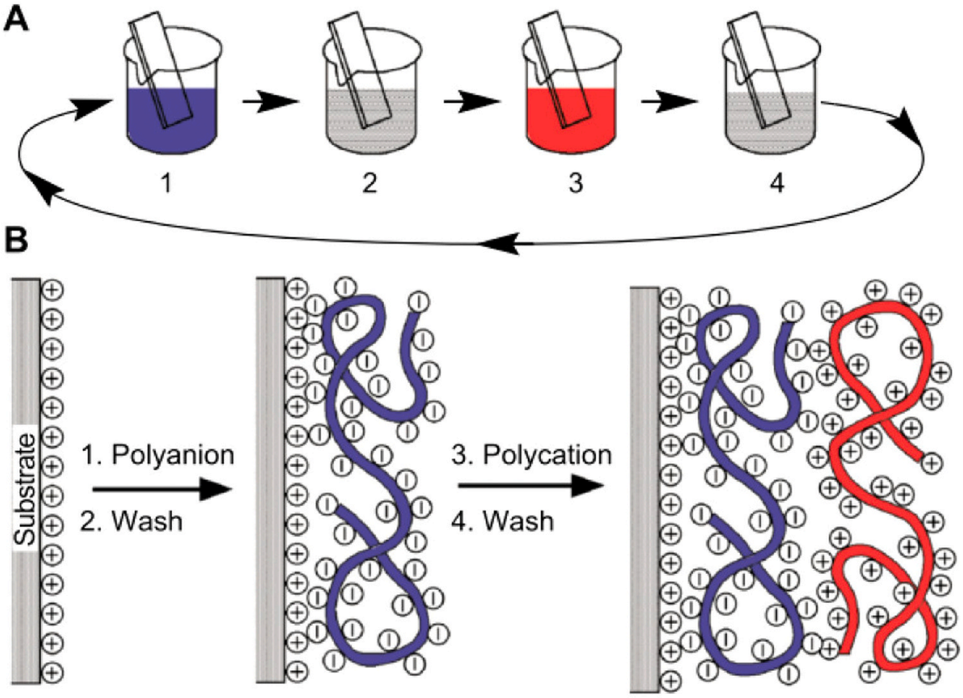

Fig. 7. General scheme of the Layer-by-Layer method: (A) Schematic illustration of immersive LbL assembly on a substrate using oppositely charged polymers, (B) the charge characteristics of the films after each deposition step. Reprinted with permission from [94]. Copyright American Chemical Society, 2016.

mechanisms. For this purpose, in general, the concept of the fire tetrahedron has been developed [73], partially replacing the well-established model of Emmons' fire triangle [74]. Compared with the latter, the fire tetrahedron considers a chain reaction as an additional contributing parameter, together with heat, oxygen, and fuel. Fuel comprises the volatile decomposition products originated from the depolymerization of the polymer bulk due to thermal exposure; oxygen supports burning due to oxidation reactions; heat is generated during combustion as the reaction is exothermic; fire is made self-sustaining due to the occurrence of a chain reaction that can propagate it through a sort of a thermal feedback continuously fueling the flame.

Specifically referring to rigid polyurethane foams, surface-engineered strategies aim to prevent one or more fire tetrahedron constituents from participating in combustion. This target can be reached by employing physical and/or chemical processes taking place in the condensed or gas phases, which are capable of (i) reducing the fuel that feeds the flame, (ii) lowering the oxygen required by the flaming combustion, (iii) dispersing the heat that interacts with the flammable material, or, finally, (iv) slowing down or even preventing the occurrence of the chain reaction [75].

Considering the action in the condensed phase [76,77], the surface treatments allow for the formation of a protective layer (acting as a physical insulating barrier directly deposited on the foam surface or chemically derived from the pyrolysis of the treated surface itself), which decreases the thermal feedback, responsible for fueling the flame, hence reducing the heat and mass transfer phenomena.

Conversely, the action in the gas phase [78] implies (i) the scavenging of the high-energy $OH^{\cdot}$ and $H^{\cdot}$ radicals by employing low-energy radicals originated from the decomposition of the coating deposited on the foam, and/or (ii) the decrease of the concentration of combustible gases through the release of such non-flammable gases as nitrogen, carbon dioxide, and water vapor [79,80].

The flame retardant effectiveness of the surface treatments applied to rigid polyurethane foams is strictly dependent on the chemistry of the deposited coatings/assemblies/complexes/colloids and on their interactions with the underlying polymer, during the application of a flame or the exposure to an irradiative heat flux. At present, most of the engineered surface treatments for rigid polyurethane foams are based on the deposition of phosphorus-, nitrogen- (or phosphorus-nitrogen)-based systems, the use of intumescent systems, and the use of nanocomposites, as described in the following.

P-based surface treatments can be active in both condensed and gas phases: in the condensed phase, they favor the formation of a stable, coherent, and protective char [81]. Conversely, in the gas phase, they decompose to such low-energy radicals as $HPO_2^{\cdot}$, $PO_2^{\cdot}$, and $PO^{\cdot}$, which promote the scavenging of $OH^{\cdot}$ and $H^{\cdot}$ radicals, hence inhibiting chain-branching reactions [82].

N-based surface treatments are typically carried out in the presence of other flame retardant additives (usually based on the phosphorus chemistry), demonstrating qualitative enhancements as far as flame suppression is considered and showing possible synergistic effects. Their action is mainly in the gas phase through the release of non-flammable gases [83].

Intumescent surface treatments involve the combination of three key components, i.e., a carbon source, an acid source, and a blowing agent [38,84]. In particular, the exposure to a direct flame or an irradiative heat source of the intumescent system triggers a series of reactions, namely involving the release of an inorganic acid that, in turn, favors the formation of a stable and coherent char in combination with the carbon source by exploiting dehydration reactions (condensed-phase action), and the release of non-flammable gases, due to the decomposition of the blowing agent, which expand the char (condensed-phase action), while diluting the gas phase.

Finally, the use of inorganic (nano)fillers (e.g., nanoclays, boron nitride, graphene and its derivatives, among others) has proven to be very effective in the design of flame retardant surface treatments for different polymer substrates, including polyurethane foams [38,75]. These (nano)fillers usually act in the condensed phase through the formation of a ceramic protective layer that confines the melt and prevents undesirable dripping phenomena [85–87].

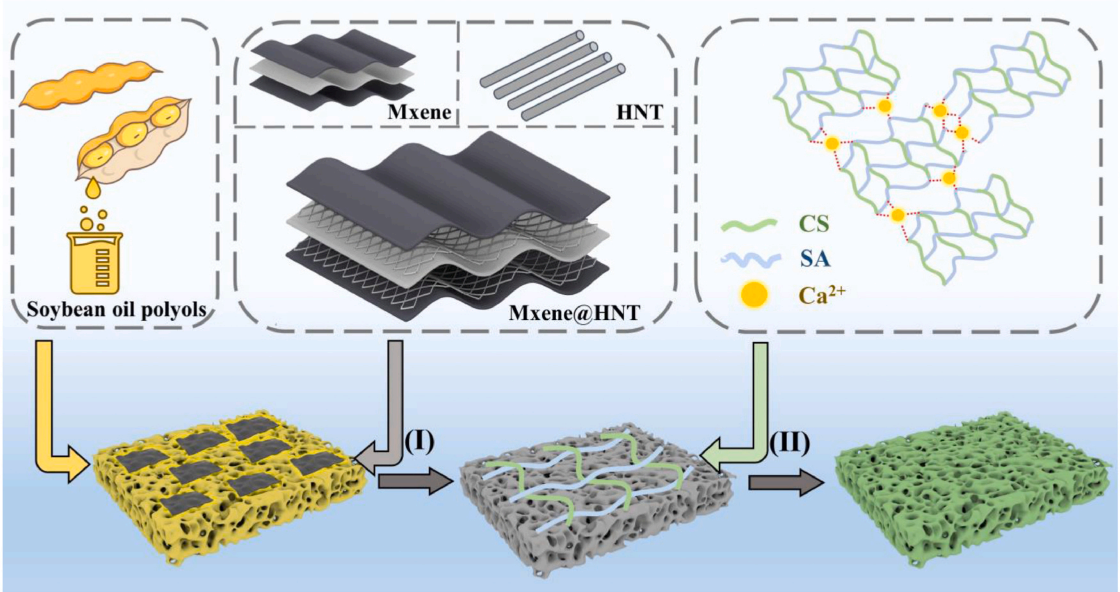

Fig. 8. Schematic diagram of the preparation of fire-retardant rigid polyurethane foams. (I) The assembly (Mxene@HNT) of Mxene and Halloysite nanotubes (HNT) was integrated onto the surface of the foam to yield a flame-retardant inner layer; (II) a dual hydrogel made of sodium alginate (SA) and chitosan (CS) using Ca^{2+} as a crosslinker was coated as the outermost layer. Reprinted with permission from [106]. Copyright Elsevier, 2024.

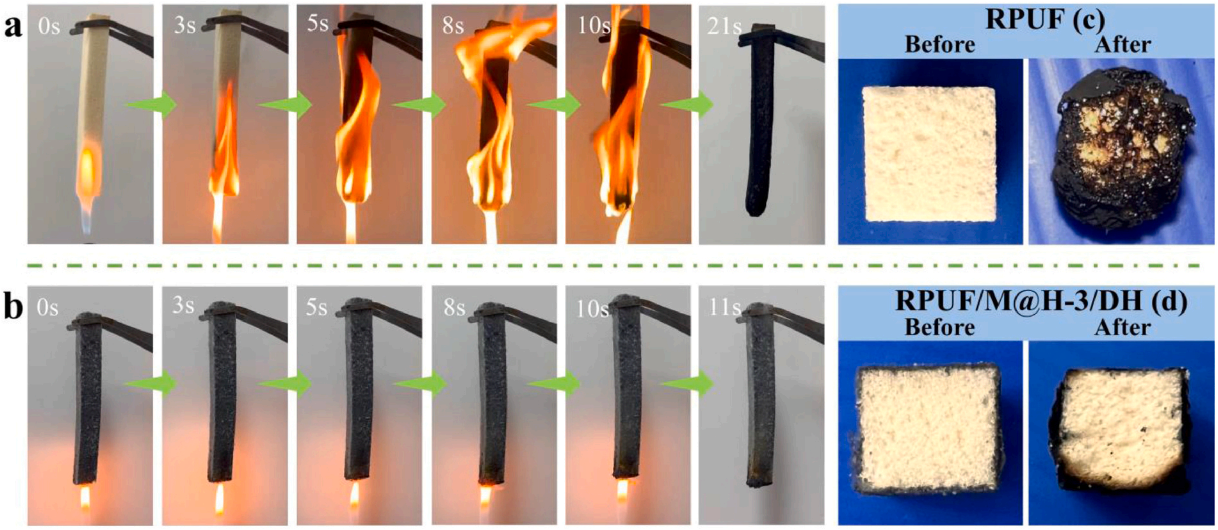

Fig. 9. Snapshots of UL-94 vertical flame spread test of the untreated polyurethane foam (RPUF, (a)) and LbL-treated counterpart (RPUF/M@H-3/DH, (b); Digital photographs of cross-section before and after combustion of RPUF (c), and RPUF/M@H-3/DH (d). Reprinted with permission from [106]. Copyright Elsevier, 2024.

5. Flame retardant surface treatments for rigid polyurethane foams: recent advances

The next sections will summarize the latest research outcomes (i.e., from 2023 to date) on the use of effective flame retardant treatments directly performed on the surface of rigid polyurethane foams. To this aim, this paragraph is organized according to three main subsections referring to layer-by-layer architectures, coatings, or “one-pot” deposited complexes/colloids.

5.1. Layer-by-layer (LbL) assemblies on rigid polyurethane foams

The LbL technique has been the subject of considerable interest from the academic community since its discovery in the late 1960s by Iler [88], and it was not until 1991 that a useful and practicable process for obtaining ultrathin multi-layered assemblies made of alternated amphiphilic polyanionic/polycationic layers was developed [89].

The deposition of a Layer-by-Layer architecture on any substrate material (including plastics, metal alloys, wood, ceramics, and composites) is generally based on the utilization of electrostatic interactions occurring between oppositely electrically charged layers [56,67,90–92]. Nevertheless, other types of interactions, like covalent bonding [93,94], hydrogen bonding [95,96], and donor/acceptor exchanges [97] can be employed. Fig. 7 shows a general scheme of the LbL technique based on electrostatic interactions.

Though the LbL method has mostly been exploited for conferring flame retardant properties to flexible polyurethane foams [98–105], the recent scientific literature reports some interesting examples related to rigid polyurethane foams, which will be described in the following.

Wang and co-workers [106] exploited an LbL process for providing excellent flame retardant features to rigid polyurethane foams. To this aim, as depicted in Fig. 8, first Halloysite nanotubes were embedded into

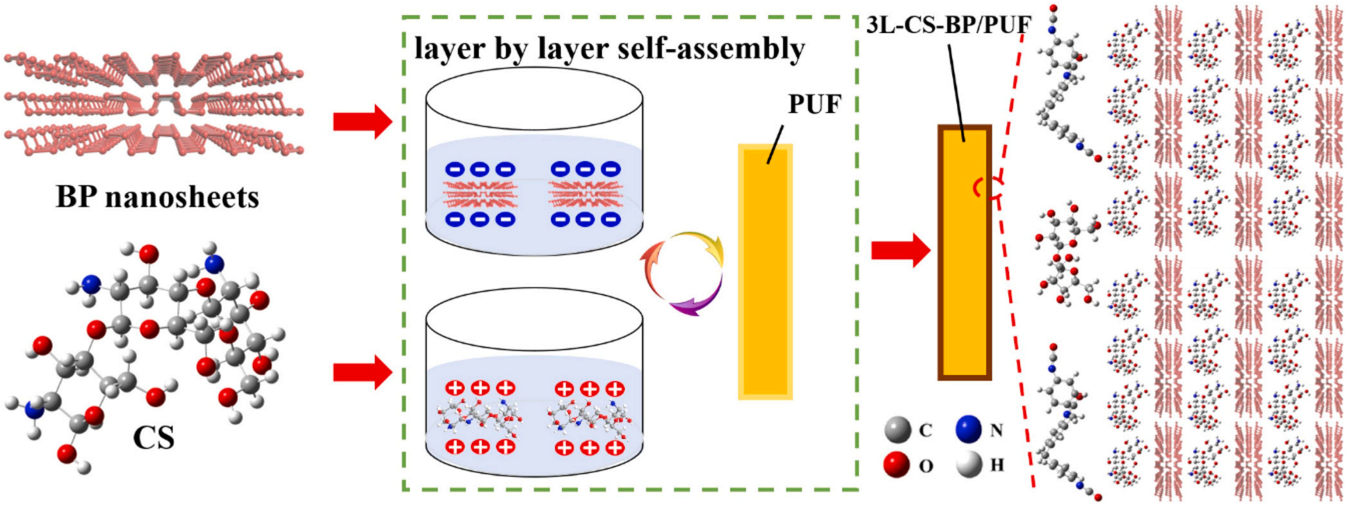

Fig. 10. Scheme of the LbL deposition of bi-layers of chitosan (CS) and black phosphorus (BP) nanosheets onto a rigid polyurethane foam (PUF). Reprinted with permission from [107]. Copyright Elsevier, 2024.

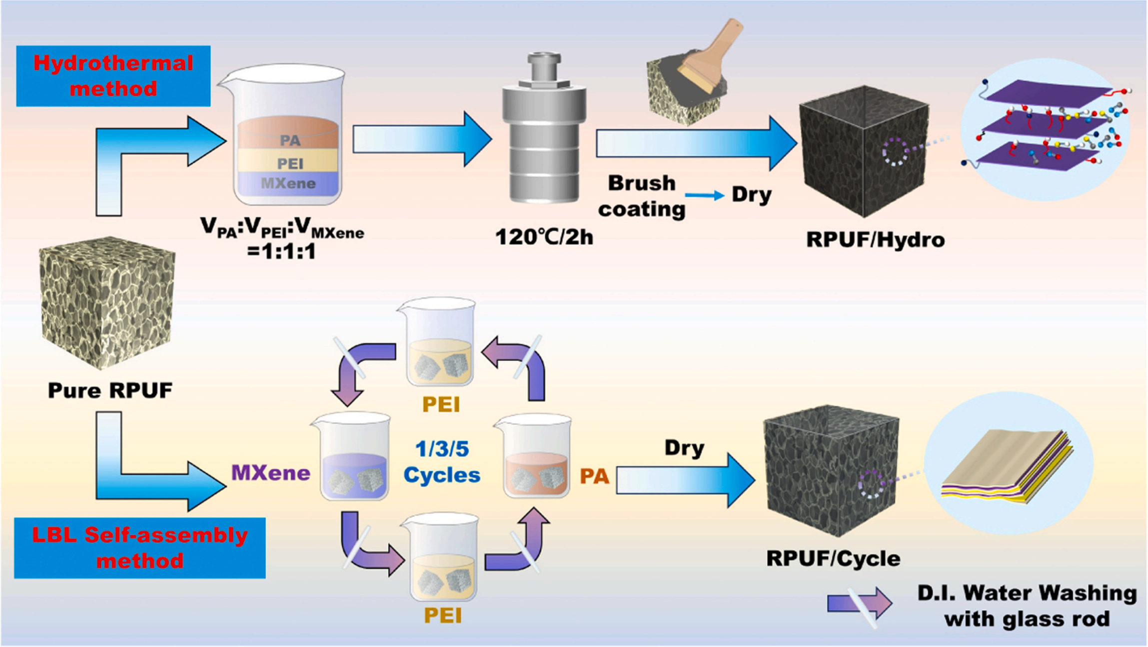

Fig. 11. Flow chart for the preparation of flame retarded polyurethane foams through LbL (the number of cycles indicates the number of quad-layers deposited) or hydrothermal method. Legend: RPUF= rigid polyurethane foam; PA= phytic acid; PEI= polyethyleneimine; D.I.=deionized. Reprinted with permission from [108]. Copyright Elsevier, 2024.

the multilayer structure of Mxene nanosheets to form a “sandwich filling” assembly. This step was repeated up to three times. The assembly was then coated onto the surface of the foam, which was subsequently treated with a dual hydrogel made of sodium alginate and chitosan using Ca^{2+} as a crosslinker. Compared to the untreated counterpart, the modified foam (after three applications of the Mxene/Halloysite nanotubes) achieved a V0 rating in vertical flame spread tests (Fig. 9); further, its LOI was as high as 30.5 % (vs. 18.6 % of the pristine foam). Finally, as assessed through forced-combustion tests (carried out 50 kW/m^2 irradiative heat flux), the LbL treatment accounted for an interesting decrease in both the peak of heat release rate (around −29 % with respect to the untreated foam) and the peak of smoke production rate (about −15 %), while showing a significant increase in carbonization yield (around +152 %). These findings were ascribed to a flame retardant action in both condensed (due to the Halloysite nanotubes/Mxene nanosheets assembly that favored the formation of a labyrinthine structure slowing down the heat and mass transfer) and gas phases (thanks to the release of water, ammonia, and nitrogen originated by the decomposition of the dual hydrogel).

Yin and co-workers [107] exploited an LbL treatment for depositing an intumescent assembly made of chitosan and black phosphorus nanosheets (up to nine bi-layers) onto a rigid polyurethane foam; the deposition is schematized in Fig. 10.

In particular, the assembly made of nine bilayers accounted for self-extinction (and V0 rate) in UL94 vertical flame spread tests, an LOI of 26.3 % (vs. 18.9 % for the untreated foam), and an important reduction in peak of heat release rate (-39.5 %) and total heat release (-28.8 %) with respect to the untreated foam (sample tested under 35 kW/m^2 irradiative heat flux). These results were ascribed to the occurrence of synergism between the two components of the LbL assembly, with the

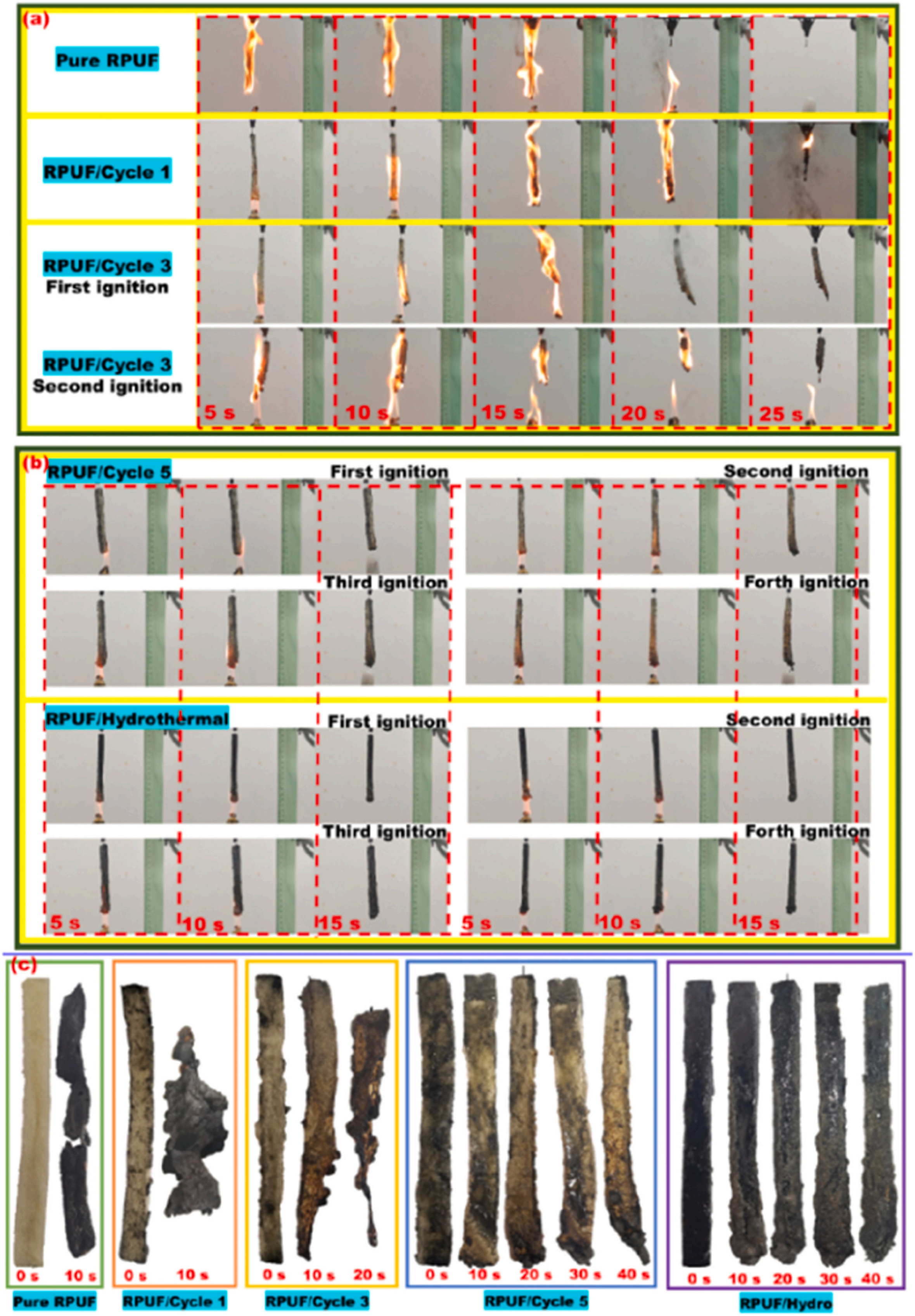

Fig. 12. (a) Snapshots from UL94 vertical flame spread tests of untreated polyurethane foam (Pure RPUF), and LbL-treated foams (RPUF/Cycle 1, RPUF/Cycle 3 - the number of cycles indicates the number of quad-layers deposited). (b) Snapshots from UL94 vertical flame spread tests of the foam treated with five quad-layers (RPUF/Cycle 5) and the foam treated with the hydrothermal coating (RPUF/Hydro). (c) Digital photographs of Pure RPUF, RPUF/Cycle 1, RPUF/Cycle 3, RPUF/Cycle 5, and RPUF/Hydro specimens with different combustion times. Reprinted with permission from [108]. Copyright Elsevier, 2024.

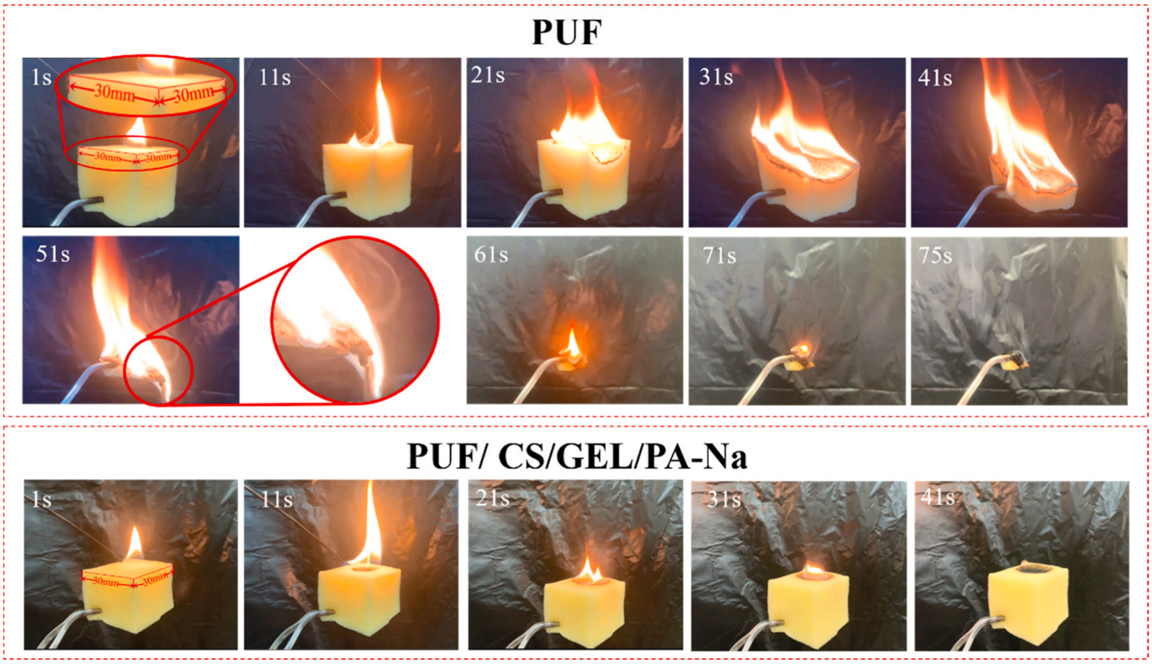

Fig. 13. Snapshots of the rigid polyurethane foams before (PUF) and after (PUF/CS/GEL/PA-Na) the application of the coating made of chitosan, gelatin, and sodium phytate. Reprinted with permission from [109]. Copyright Elsevier, 2023.

formation of P-O-C structures (i.e., P-containing esters) with high charring activity in the condensed phase, as well as to the free radical scavenging effect exerted by the P-O radicals in the gas phase.

In a further research effort, Li and co-workers [108] compared the fire behavior of coatings made of MXene, polyethyleneimine, and phytic acid, deposited onto a rigid polyurethane foam either through Layer-by-Layer (up to five quad-layers with the sequence: MXene/polyethyleneimine/phytic acid/ polyethyleneimine) or hydrothermal method (introducing MXene colloidal suspension (5 mg/ml), phytic acid solution (50 wt%), and polyethyleneimine solution (50 wt%) into an autoclave at 1:1:1 ratio, Fig. 11). Regardless of the type of synthesis method, the concurrent presence of the three constituents accounted for the occurrence of synergistic flame retardant activity both in condensed (thanks to the dehydration effect exerted by phytic acid, in combination with the ceramization of MXene) and gas (through the formation of PO· radicals and N_2) phases. In particular, as assessed through vertical flame spread tests, the deposition of five quad-layers, or the coating obtained by the hydrothermal treatment, accounted for the self-extinction (and V0 rating) of the rigid polyurethane foam specimens (Fig. 12). Besides, forced-combustion tests performed at 35 kW/m^2 highlighted a better performance of LbL treatments compared to the hydrothermal coatings in terms of reduction of peak of heat release rate (about −16 % vs. −5.4 % for LbL and hydrothermal coatings, respectively) and total smoke release (about −92 % vs. −90 % for LbL and hydrothermal coatings, respectively), with the untreated foam considered as the reference.

In summary, this section has provided some recent examples of the potential offered by LbL treatments on rigid polyurethane foams. It is worth noting that the deposited assemblies are able to significantly improve the fire resistance of the treated substrates. Moreover, the wide choice of the type of constituents of the layers, the tunable number of deposited layers and the structure (bi-layered, quad-layered) of the deposited architectures make the LbL method very attractive and suggest its further implementation in the coming years. However, despite the flame-retardant efficacy of LbL, this technique is still limited to laboratory-scale applications and would greatly benefit from scale-up to pilot/industrial scale for a possible market exploitation. In addition, none of the above case studies discussed the durability of LbL treatments, which could represent a significant limitation, as the flame retardant effects would be expected to be of limited duration.

5.2. Flame retardant coatings on rigid polyurethane foams

Most of the current research on surface flame retardant treatments for rigid polyurethane foams focuses on the design, application, and characterization of effective coatings. The latest research outcomes will be summarized in the following.

Tang et al. [109] designed a "green" coating comprising chitosan, gelatin, and sodium phytate; the coating was then applied to a rigid polyurethane foam, utilizing a rolling procedure. The presence of the coating accounted for the self-extinction of the coated foams in open-flame tests (Fig. 13).

Further, as revealed by cone calorimetry tests carried out at 50 kW/m^2 irradiative heat flux, the surface treatment was responsible for a significant decrease in both peak of heat release rate (-53.5 % compared to the untreated foam) and total heat release (-48.5 %). These findings were ascribed to a substantial flame retardant action of the coating in the condensed phase through the formation of stable, coherent, and protective char (Fig. 14).

Han and co-workers [110] exploited a combined strategy of nano-reinforcement and surface treatment for obtaining multifunctional rigid polyurethane foams. In particular, the nano-reinforcement relied on the incorporation of nanosheets of phosphazene-phytic acid into the polymer matrix at a very low loading (i.e., 3 wt%). After having been nano-reinforced, the foam was surface treated with a coating comprising polydopamine-encased ammonium polyphosphate, polyethyleneimine, and 1-octadecanethiol-wrapped polydopamine. A V0 rating was observed in UL94 vertical flame spread tests performed on the coated foam that also exhibited an LOI of 42.5 % (vs. 19.3 % for the pristine foam). Besides, forced combustion tests (irradiative heat flux: 35 kW/m^2) highlighted a significant decrease in the peak of heat release rate (about −44 % compared with the pristine foam) and in the total heat release (about −30 %), together with a remarkable increase in the final residue (+507 %). All these findings were attributed to i) the charring ability of the nanosheets of phosphazene-phytic acid and polydopamine, ii) the intumescent character provided by ammonium

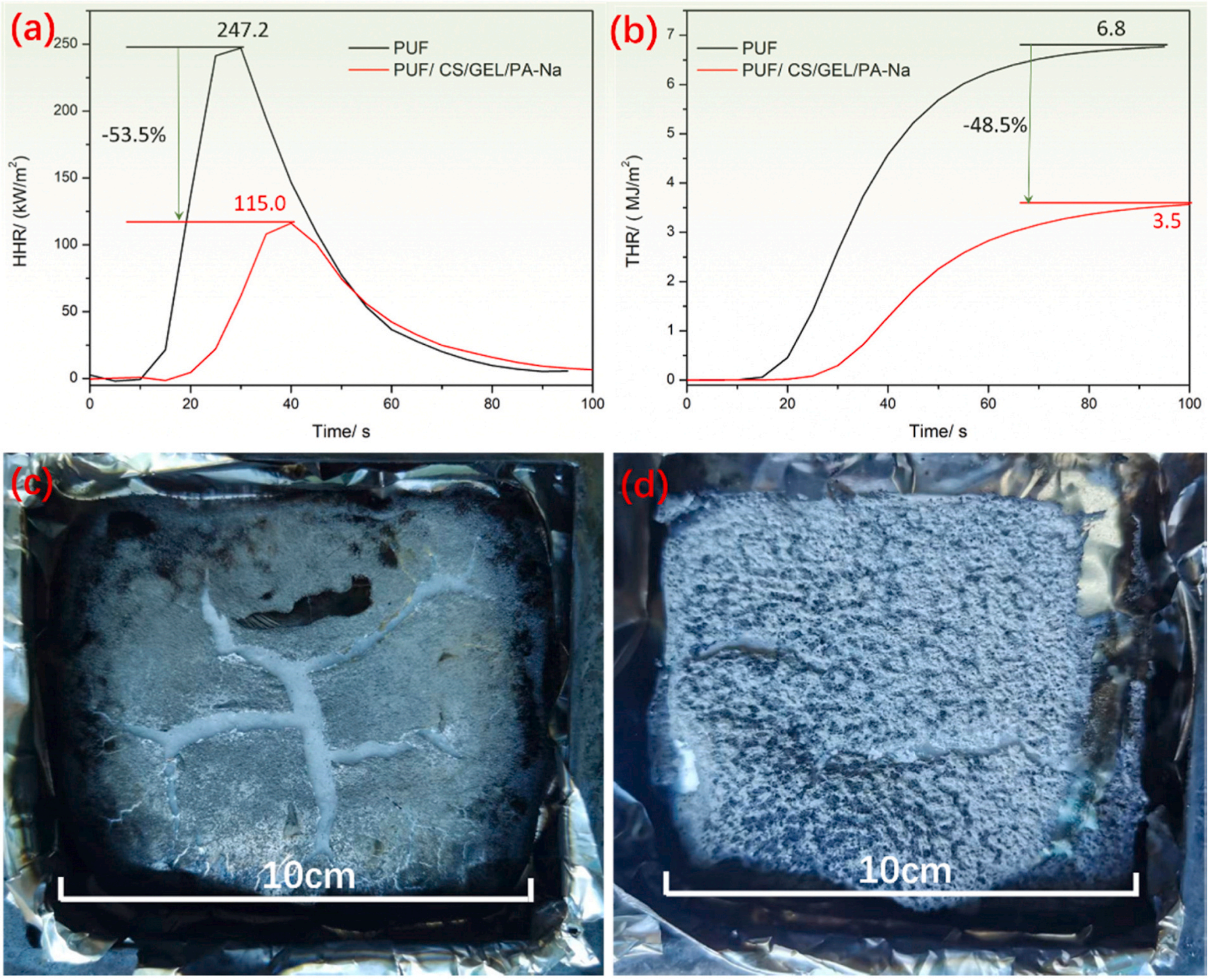

Fig. 14. Results from cone calorimetry tests (50 kW/m^2 irradiative heat flux): comparison between Heat Release Rate (HRR (a)) and Total Heat Release (b) vs. time curves for the pristine foam (PUF) and the treated counterpart (PUF/CS/GEL/PA-Na); residues of the foams at the end of the test, before (c) and after (d) the application of the coating. Reprinted with permission from [109]. Copyright Elsevier, 2023.

polyphosphate and polyethyleneimine, and iii) the free radical scavenging effect of polydopamine. Finally, it is worth noticing that the deposited coating conferred a good hydrophobicity (with static water contact angles of about 137°), without affecting the thermal conductivity of the foams.

Zhang and co-workers [86] synthesized a coating containing a phenolic resin, 9,10-dihydro-9-oxa-10-phosphazephenanthrene-10-oxide (DOPO), and nano-SiO_2 (from 2 to 8 wt%) and applied it onto a rigid polyurethane foam using a glass rod. A schematic of the process is shown in Fig. 15.

Selecting a 2:1 DOPO:nanoSiO_2 in the coating formulation accounted for the achievement of V0 rate and self-extinction in vertical flame spread tests, regardless of the nano-silica loading. Further, the presence of 8 wt% of nanosilica allowed for reaching LOI values as high as 28.1 % (vs. 18.2 % for the uncoated foam). Finally, as assessed by forced-combustion tests (performed at 35 kW/m^2 irradiative heat flux), compared with the pristine foam, the incorporation of the highest nanosilica loading into the deposited coating was responsible for a remarkable decrease in both peak of heat release rate and total heat release (by 47 and 36.5 %, respectively). These findings were attributed to the high char-forming character of the phenolic resin in combination with DOPO, as well as to the ceramization effect promoted by the nanoSiO_2.

Recently, Yu et al. [112] synthesized a UV-curable green, intumescent coating formulation consisting of D-sorbitol (carbon source), phytic acid (acid source), and glycine (gas source). A schematic representation of the synthetic route is sketched in Fig. 16.

UL94 vertical flame spread tests highlighted self-extinction and V0 rate for the coated polyurethane foam, which also exhibited an LOI as high as 39.7 % (vs. 20.2 % of the uncoated foam); besides, as assessed by forced combustion tests (carried out at 50 kW/m^2), the flame retarded foam showed an increased time to ignition (from 2, control foam, to 5 s), as well as decreased peak of heat release rate (by about 60 %) and total smoke production (by about 21 %). These findings were ascribed to the intumescent effect of the UV-curable coating.

Huang et al. [113] designed a flame retardant, biomimetic, and supramolecular (though extended hydrogen bonding) nano-coating made of tannic acid-functionalized hexagonal boron nitride nanosheets (obtained through a ball milling exfoliation method), tannic acid, and polyvinyl alcohol. The treated foams were self-extinguishing and V0-rated in UL94 vertical flame spread tests. In addition, compared to the uncoated counterpart, the deposited coating accounted for a significant lowering in peak of heat release rate (about −52 %) and peak of smoke production rate (around −53 %), hence demonstrating a high flame retardant effect on the underlying polymer matrix.

Fang and co-workers [114] employed a radical polymerization reaction to synthesize four types of sulfur-containing copolymers (starting from vinyl sulfonic acid sodium, ethylene sulfonic acid sodium, and sodium p-styrene sulfonate, in combination with 2-hydroxyethyl acrylate or 4-hydroxybutyl acrylate). In particular, the poly(ethylene

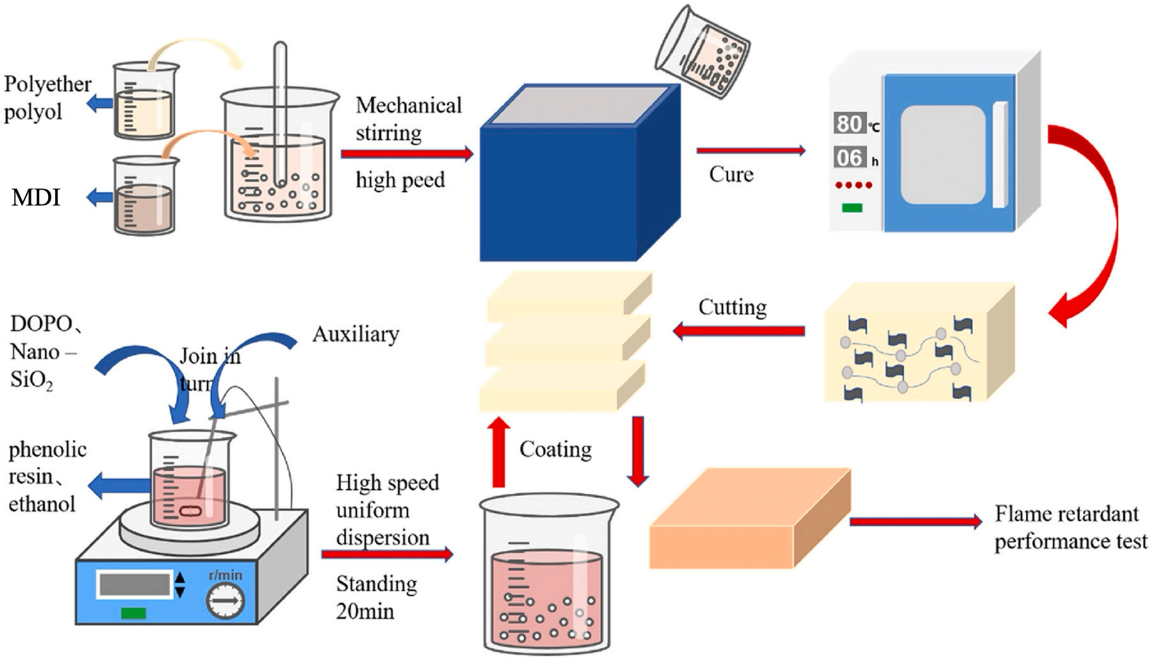

Fig. 15. Experimental flowchart for the preparation of flame retarded rigig polyurethane foam. Legend: DOPO= 9,10-dihydro-9-oxa-10-phosphazephenanthrene-10-oxide; MDI=polyisocyanate. Auxiliary includes dispersant, thickener, and defoamer. Reprinted with permission from [111]. Copyright Wiley, 2023.

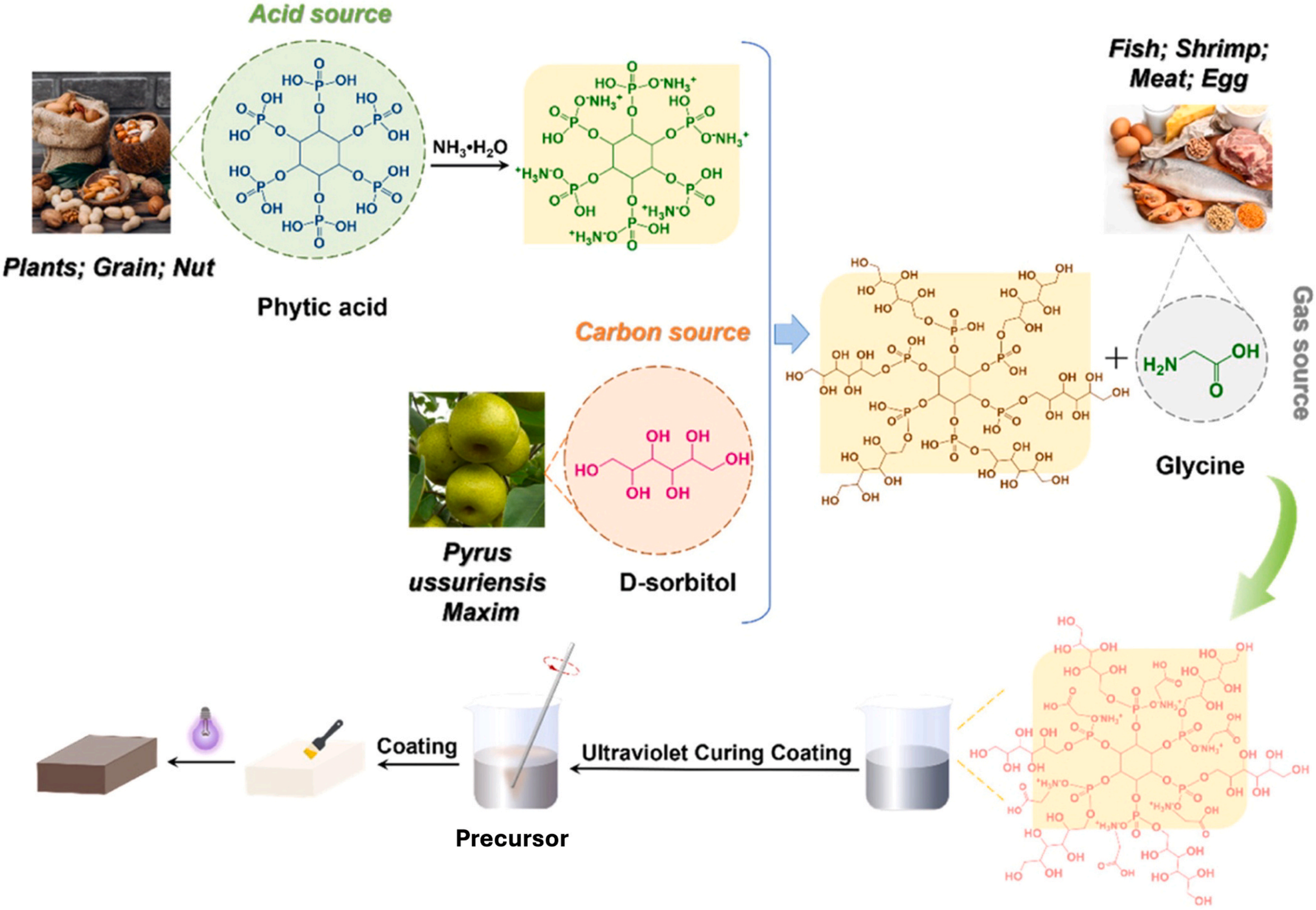

Fig. 16. Synthesis of a UV-curable green, intumescent coating formulation and its application to rigid polyurethane foam. Reprinted with permission from [112]. Copyright Elsevier, 2024.

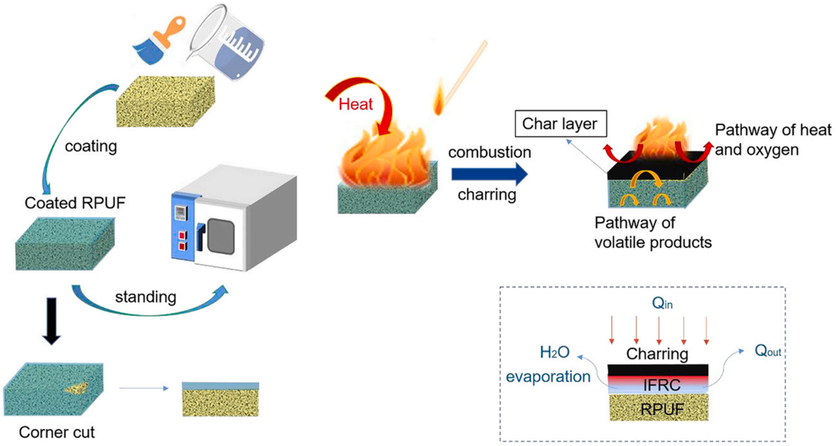

Fig. 17. Flame-retardant mechanism of a rigid polyurethane foam (RPUF) coated with intumescent coating (IFRC) made of a silicone acrylate emulsion incorporating ammonium polyphosphate-pentaerythritol-melamine, γ-aminopropyl triethoxysilane-functionalized montmorillonite, aluminum hydroxide, and titania. Reprinted with permission from [115]. Copyright Wiley, 2024.

sulfonic acid sodium-*co*-2-hydroxyethyl acrylate) coating showed the best fire retardant performance when coated on the rigid polyurethane foam. In particular, a thickness of 600 µm of this coating ensured a V0 rating in UL94 vertical flame spread tests, together with an LOI as high as 36.4 % (vs. 19.1 % for the control foam). Further, this coating was responsible for a significant increase in the time to ignition (from 4 - uncoated foam, to 35 s) and a considerable decrease in peak of heat release rate (by about 34 %), as assessed by cone calorimetry tests (irradiative heat flux: 35 kW/m^2).

Zhang et al. [115] designed an intumescent coating based on a silicone acrylate emulsion (as a film-forming system), embedding ammonium polyphosphate-pentaerythritol-melamine, γ-aminopropyl triethoxysilane-functionalized montmorillonite, aluminum hydroxide, and titania. In particular, an optimized formulation containing 25 wt% silicone acrylate, 5 wt% modified montmorillonite, 6 wt% aluminum hydroxide, and 4 wt% titanium dioxide accounted for self-extinction (and V0-rating) in UL94 vertical flame spread tests, as well as for a significant decrease in the peak of heat release rate (by about 58 %), total heat release (by around 74 %), and total smoke production (by around 64 %) with respect to the uncoated foam, as revealed by cone calorimetry tests (50 kW/m^2 irradiative heat flux). This excellent fire behavior was ascribed to the charring ability of the intumescent coating, the dilution effect in the gas phase exerted by the decomposition products during combustion, and the smoke-suppressant features of aluminum hydroxide (Fig. 17).

Wang and co-workers [37] exploited a free radical thermal curing for designing a flame retardant coating derived from a phosphorous-containing prepolymer obtained from the ring-opening reaction of 2–hydroxyethyl methacrylate phosphate and glycidyl methacrylate (Fig. 18).

The deposition of the coating accounted for self-extinction and V0-rating; moreover, LOI value increased up to 27.8 % (vs. 19 % for the control foam). As assessed by forced-combustion tests performed at 35 kW/m^2 irradiative heat flux, the coated samples showed significantly decreased total heat release and peak of heat release rate values (by about 80 and 55 %, respectively) compared with the uncoated counterparts. Besides, the high flame retardancy conferred by the deposited coating was witnessed by the results of continuous burning tests (Fig. 19). These findings were interpreted based on a flame retardant mechanism involving the condensed (through the formation of a protective char) and gas (through free radical scavenging) phases. Finally, it is noteworthy that the coating did not affect the overall thermal conductivity of the foam but ameliorated its compression strength and water resistance.

In summary, this section has provided some recent examples of the potential offered by the deposition of flame retardant coatings on rigid polyurethane foams. Compared to LbL and the surface treatments with complexes/colloids, this strategy is the most well-established and shows some advantages. In particular, regardless of its usually high effectiveness in providing rigid polyurethane foams with flame retardant features, it would be easily scalable, also taking into account the opportunity of using already available coating plants. Further, it is worth noting that the possibility of exploiting thermal or UV-curable coatings provides the deposited coatings with durability.

5.3. *“One-pot” flame retardant complexes/colloids deposited on rigid polyurethane foams*

This particular strategy applied to rigid polyurethane foams is still in its infancy, although some interesting (and promising) examples have recently been reported in the scientific literature.

Sun et al. [116] designed an organic-inorganic polymer colloid based on ammonium polyphosphate and carboxymethyl chitosan, which was applied to a rigid polyurethane form by using a UV-curing technology. The treated polyurethane foam achieved self-extinction (and V0 rate) in UL94 vertical flame spread tests; besides, its LOI value was as high as 42.6 % (vs. 20.3 for the control foam, Fig. 20).

As assessed by cone calorimetry tests, the treated foams showed an increased time to ignition (from 2 – control foam – to 17 s) and final residue (from 0.4 – control foam – to 10.7 %), together with a decrease in peak of heat release rate (by about 11 %, compared with the untreated counterpart). These outcomes were explained in terms of a “double” flame retardant mechanism (Fig. 21) involving both the condensed and gas phases (through a charring effect induced by the applied colloid and a dilution effect, respectively).

Luo and co-workers [117] exploited a Cu^{2+}-assisted aqueous phase separation for *in situ* assembling a nanostructured polyelectrolyte coating made of carboxymethyl chitosan and ammonium polyphosphate on rigid polyurethane foam. The presence of the coating accounted for self-extinction and V0-rate in UL94 vertical flame spread tests; in addition, compared with the control foam, the modified counterpart reached a 36 % LOI value (vs. 18 %).

Finally, as revealed by forced-combustion tests (carried out at 35 kW/m^2), compared with the control foam, the flame retardant assembly allowed for a decrease in the thermal parameters (about 63 and 26 % reduction in peak of heat release rate and total heat release, respectively), as well as in the smoke parameters (around 66 and 30 % decrease in smoke production rate and total smoke production, respectively). These findings were attributed to an extended char-forming activity catalyzed by Cu^{2+} ions in the condensed phase and a dilution

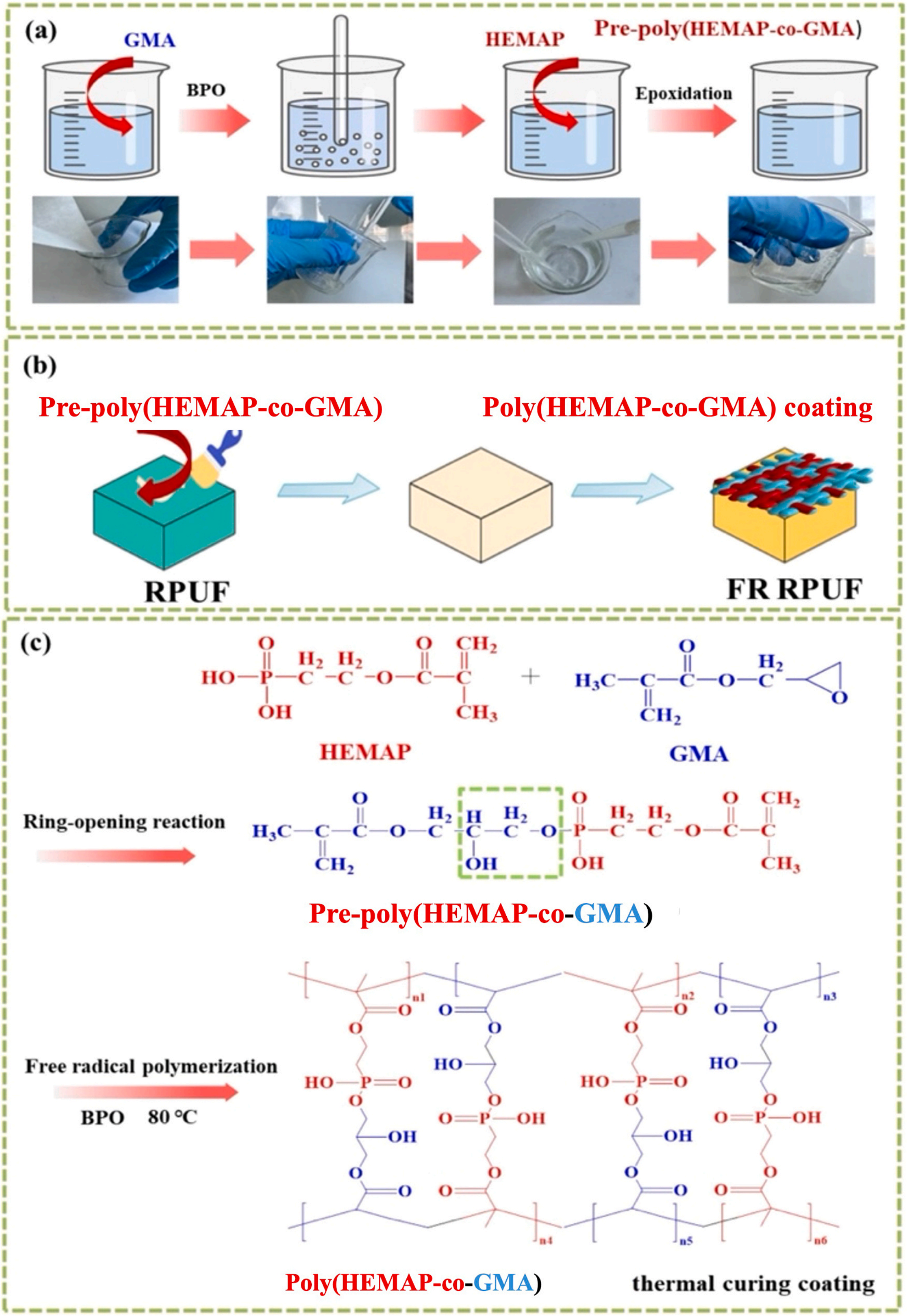

Fig. 18. (a) Schematic diagram of the preparation of a phosphorous-containing prepolymer; (b) Schematic diagram of the prepolymer coating on the rigid polyurethane foam (RPUF); (c) Scheme of the synthesis of the prepolymer and the final polymer. Legend: BPO=Benzoyl peroxide; GMA=glycidyl methacrylate; HEMAP= 2-hydroxyethyl methacrylate phosphate; pre-poly(HEMAP-co-GMA)=prepolymer; poly(HEMAP-co-GMA)=polymer; FR RPUF=flame retardant rigid polyurethane foam. Reprinted with permission from [37]. Copyright Elsevier, 2024.

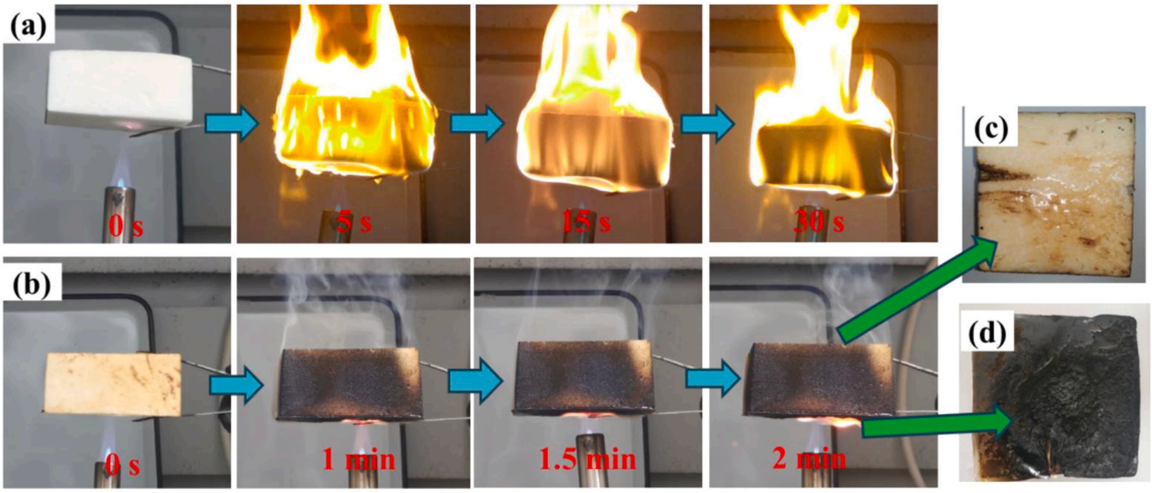

Fig. 19. Video screenshots of the uncoated foam (a), and the foam coated with the P-containing polymer (b) during continuous burning test; Photograph of the top surface (c) and bottom surface (d) after the test. Reprinted with permission from [37]. Copyright Elsevier, 2024.

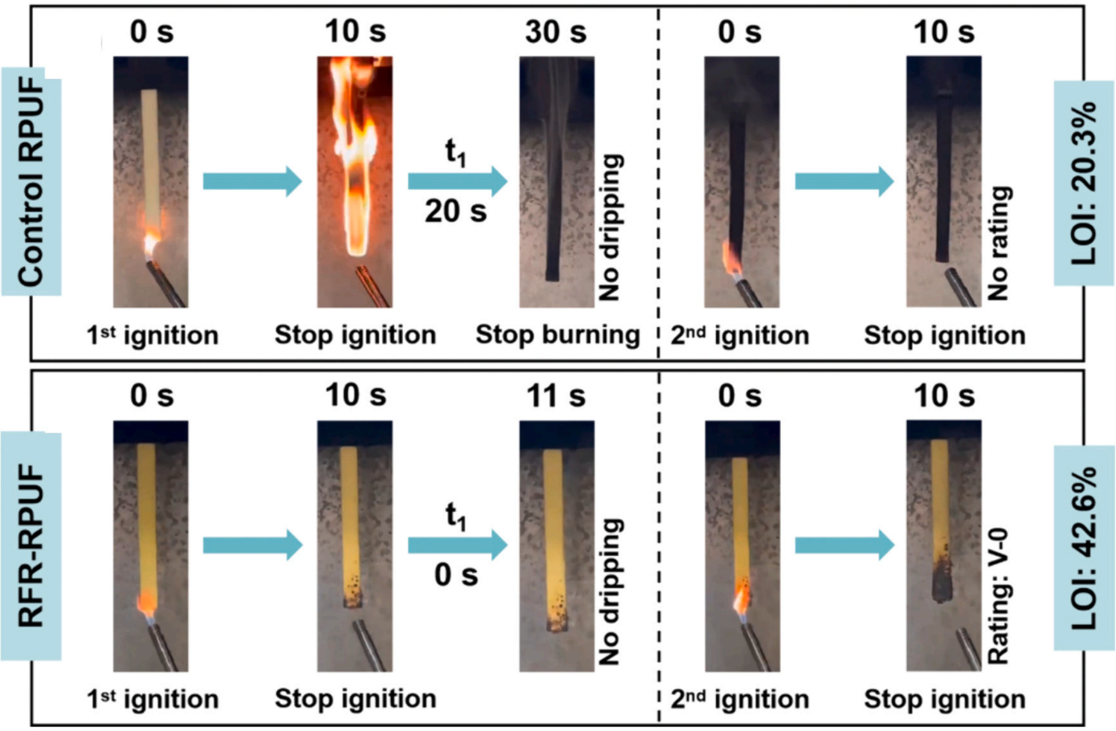

Fig. 20. Snapshots of UL94 vertical flame spread tests performed on the polyurethane foam before (Control RPUF) and after (RFR-RPUF) the application of the organic-inorganic polymer colloid based on ammonium polyphosphate and carboxymethyl chitosan. Reprinted with permission from [116]. Copyright Elsevier, 2024.

effect in the gas phase (Fig. 22).

In summary, as mentioned at the beginning of this section, the “one pot” deposition of complexes and colloids, while very interesting, remains largely unexplored for several reasons. Firstly, it is newer compared with the other two surface-engineered strategies. In addition, the formulation of colloids and complexes is often challenging due to limited availability of ingredients and potential instability issues of the designed formulations. Furthermore, like LbL, the durability of these treatments has not been investigated yet. However, it can be foreseen that this method will undergo further developments and implementations for the coming years to disclose its high potential in flame retardancy.

Finally, Table 2 compares the three surface-engineered methods discussed in the previous sections, highlighting their main characteristics, advantages and drawbacks specifically related to their current use for the surface treatment of rigid polyurethane foams.

6. Conclusions and perspectives

In the civil engineering and construction sector, the use of high-performing materials is almost always associated not only with relevant thermal and mechanical performance but also with safety and environmental concerns. In particular, the need for the exploitation of fireproof materials is becoming more and more mandatory, partly in

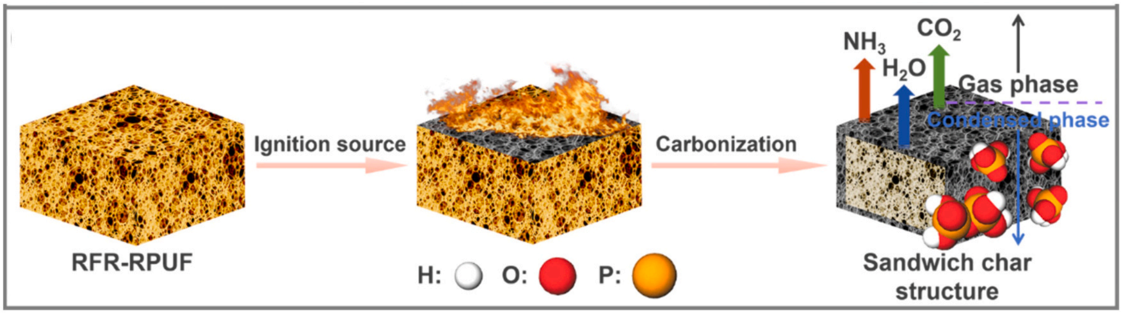

Fig. 21. Flame retardant mechanism for the rigid polyurethane foam (RFR-RPUF) treated with the organic-inorganic polymer colloid based on ammonium polyphosphate and carboxymethyl chitosan. Reprinted with permission from [116]. Copyright Elsevier, 2024.

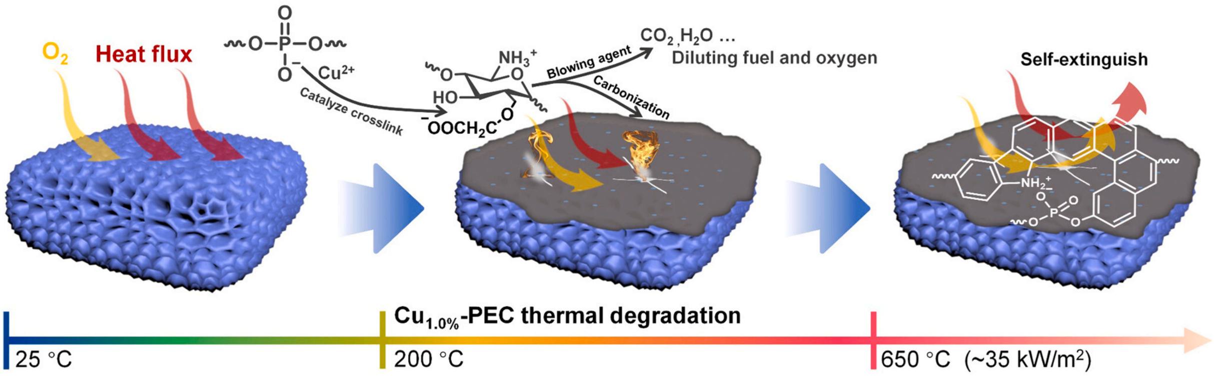

Fig. 22. Flame retardant mechanism for the rigid polyurethane foam treated with the nanostructured polyelectrolyte complex ($Cu_{1.0\ \%}$-PEC) made of carboxymethyl chitosan and ammonium polyphosphate. Reprinted with permission from [117]. Copyright American Chemical Society, 2024.

Table 2
Comparison among the three surface-engineered methods.

Surface-engineered method	Pros.	Cons.
Layer-by-layer assembly	∘ Wide choice of components (even bio-based) ∘ Possibility of using waterborne dispersions/solutions ∘ High flame retardant effectiveness	∘ Typically, time-consuming depositions ∘ Unexplored durability ∘ Suitability for laboratory application only
Coating deposition	∘ Wide choice of components (even bio-based) ∘ High flame retardant effectiveness ∘ Quite fast deposition processes ∘ Possibility of designing solvent-free formulations ∘ Possibility of designing treatments exhibiting environmental resistance ∘ Potential suitability for industrial applications	∘ Limited availability of waterborne formulations ∘ Possible limited durability (in terms of abrasion resistance)
One pot deposition of complexes/colloids	∘ High flame retardant effectiveness ∘ Short deposition time (i.e., fast processes)	∘ Unexplored durability ∘ Limited availability of ingredients for the formulations ∘ Potential instability of the formulations ∘ Suitability for laboratory application only

response to directives and regulations that have been promulgated in recent years. In this context, rigid polyurethane foams are undergoing a period of strong technological innovation aimed at improving their flame retardance performance but without significantly impacting their mechanical and thermal properties.

As described in the present review paper, the surface modification strategy has significant advantages over bulk treatments in that it does not interfere with the expansion process of the foam and allows the flame retardant additive to be concentrated on the very surface of the material, where it must perform its function. In addition, flame retardant surface treatments allow the use of the minimum amount of additives and avoid the need to incorporate them within the mass of the material to be protected, thereby also limiting the overall economic cost of the process.

Despite the above advantages, the use of surface treatments is still somehow limited because of several reasons that will be explained in the following.

First, all the proposed surface treatments described are the result of laboratory research activities: any exploitation, at least at the preindustrial level, requires a significant scale-up, which as yet has not proved possible.

Then, despite some significant efforts toward the use of low environmental impact components/formulations, several flame retardant surface treatments are still mainly based on “conventional” chemistries, which may necessitate the use of solvents and chemicals that are far from being environmentally friendly. Therefore, new bio-sourced flame retardant additives that possibly exploit “greener” chemical products and are suitable for surface treatments should be explored, assessed and optimized.

A further limiting factor that may exhibit quite a high impact on the exploitation of flame retardant surface treatments for rigid polyurethane foams relies on the durability of these surface treatments: indeed, the high flame retardant performance should be guaranteed for the whole life of the component. As a matter of fact, some factors that significantly limit durability concern not only the usually poor environmental resistance (humidity) of some surface treatments but also the limited mechanical strength (especially abrasion resistance), which certainly restricts their potential for use.

However, it is believed that the research activities undertaken on this topic can progress in the coming years, broadening the research insights and further improving surface technologies.

CRediT authorship contribution statement

Giulio Malucelli: Writing – review & editing, Writing – original draft, Supervision, Methodology, Funding acquisition, Data curation, Conceptualization.

Declaration of Competing Interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.conbuildmat.2025.140947.

Data availability

No data was used for the research described in the article.

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