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Thin coatings for fire protection: an overview of the existing strategies, with an emphasis on layer-by-layer surface treatments and promising new solutions

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Abstract

Catastrophes due to fires cause a lot of material damages and the loss of many human lives. They have been rising in number and severity over the years because of the extensive use of flammable materials such as polymers, which is why it is necessary to design strategies to limit their flammability. Most commercial solutions rely on adding molecules called fire retardant in the bulk of the polymers. On the other hand, concerns regarding the health and environmental hazards of this type of treatments have been growing among both the scientific community and the general public, and regulations were strengthened in response. In this context, fire retardant surface treatments have attracted a lot of the attention recently as they allow to concentrate the fire retardant effect at the interface between the material and the flame, that is, where the combustion process appears. Coatings with thicknesses ranging from the dozens of nanometers to a few micrometers are favored as they limit the amount of material used and limit the impact on the functional properties of the material. This review aims at giving an overview of the different strategies for developing thin coatings for fire protection, with a special emphasis on layer-by-layer surface treatments, which is one of the most promising solutions being developed. One pot strategies as well as several opportunities for new designs are also proposed in order to give some perspectives and new ideas on the development of novel systems.

1. Introduction

Polymeric materials are widely used due to their specific advantageous properties. They are light, durable, resistant to corrosion and they offer mechanical properties unreachable with other types of materials. They are present everywhere in our daily environment, for example in indoor furniture and upholstery, household appliances, building insulation, electric cables insulation, outdoor infrastructures and furniture or disposable tableware and containers. They are also used in more technical applications such as airplanes, automotive, rail, energy or space industries, raw or as composites. However, their organic nature makes them highly inflammable, and several catastrophes can attest of the danger their use can pose if this property is not properly considered. Statistics for the year 2018 in France show that 305 500 safety interventions were due to fires, causing 26 253 victims including 262 deaths.[1] World's statistics compiled from 34 countries by the CTIF report 3,2 million fires in 2017, resulting in 16 900 fire deaths.[2] The Grenfell tower tragedy that costed 72 lives in June 2017 is still fresh in the minds of people living in Occidental Europe.

This shows how necessary it is to lower the flammability of organic materials. In a way, it would be logical to design materials that are not flammable. For example, high performances polymers such as PEEK (polyetherether ketone) and PBO (polybenzoxazole) have an intrinsic low flammability. However, this solution is costly and often implies difficult processes. Another solution is to add fire retardant molecules in the formulation of the polymer, but this solution also poses other problems in terms of matrix compatibility, change of mechanical properties, or environmental and human toxicity. For these reasons, surface fire retardant treatments have attracted some of the attention. This is a relevant approach as it allows to concentrate the fire retardant effect at the interface between the material and the environment, that is, where it is needed. Moreover, less material is used, and there is no compatibility problem with the matrix. Thin fire retardant coatings especially are the subject of a high number of investigations, as they demonstrate high efficiency with very small thicknesses, and therefore fewer materials needed.

This review aims at giving the reader an overview of the different fire retardant thin coatings designed to this day. The combustion of polymers and strategies for polymers fire retardancy are presented in a first part, and the relevancy of thin coatings as a fire protection is stressed out. In a second and third part, flame retardant surface treatment made via sol-gel and plasma-assisted synthesis are reviewed. A special emphasis was made on the design of thin coatings

via layer-by-layer technology in a fourth part, as it is one of the most promising and studied technology. Opportunities for new designs as well as future trends are proposed in a fifth part and discussed as a conclusion.

2. Polymers combustion and fire retardancy

Polymer combustion is a complex and self-sustaining mechanism, involving reactions both in the condensed and gas phase, that is driven by heat and mass transfer at the interface between the material and the flame. Under high temperatures, polymers undergo thermal decomposition. Thermo-oxidative reactions also take place in the presence of oxygen. Both yield small volatile molecules as well as radical species, highly likely to be very reactive, especially those evolved from the reaction with oxygen. When they are released into gas phase, they form an inflammable mixture with air, which will combust if the temperature is high enough (above ignition temperature) or in the presence of an external source of energy such as a spark or an electric arc, for example. Combustion of the reactive species with oxygen creates light (whose emission spectrum depends on the species present in the flame) and is exothermic. The resulting heat feedback to the material will help sustaining the polymer combustion reaction until oxygen or flammable mass are depleted. Further products from the thermal decomposition and thermo-oxidative reactions might not be volatile, which can contribute to limit the amount of flammable products, mainly by forming a stable carbonaceous layer called char. The combustion process of polymers is summarized in Figure 1.

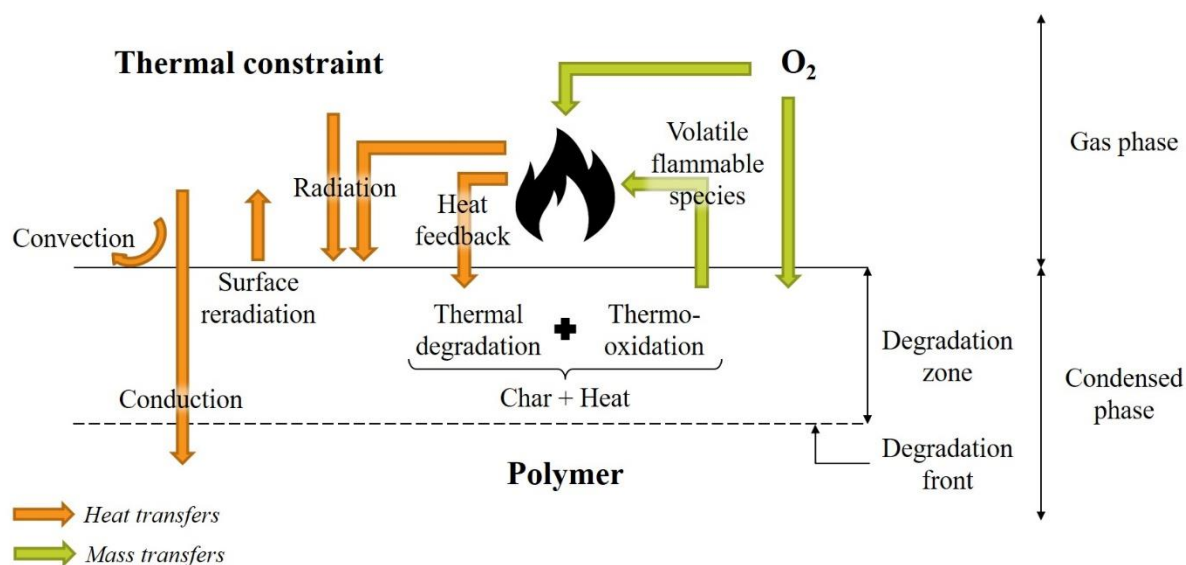


Figure 1. Polymer combustion mechanism.

Methods to fire protect polymers act on at least one of the elements of the diagram. The first method consists in synthesizing a polymer intrinsically resistant to thermal decomposition, or whose decomposition yields a thermally stable residue. For example, high performance polymers, such as PolyEther Imide, PolyEtherEtherKetone (PEEK), PolyImide (PI), PolyBenzOxazole (PBO), etc., have high decomposition temperatures, as well as in some cases a high char yield, which makes them intrinsically fire resistant.[3]

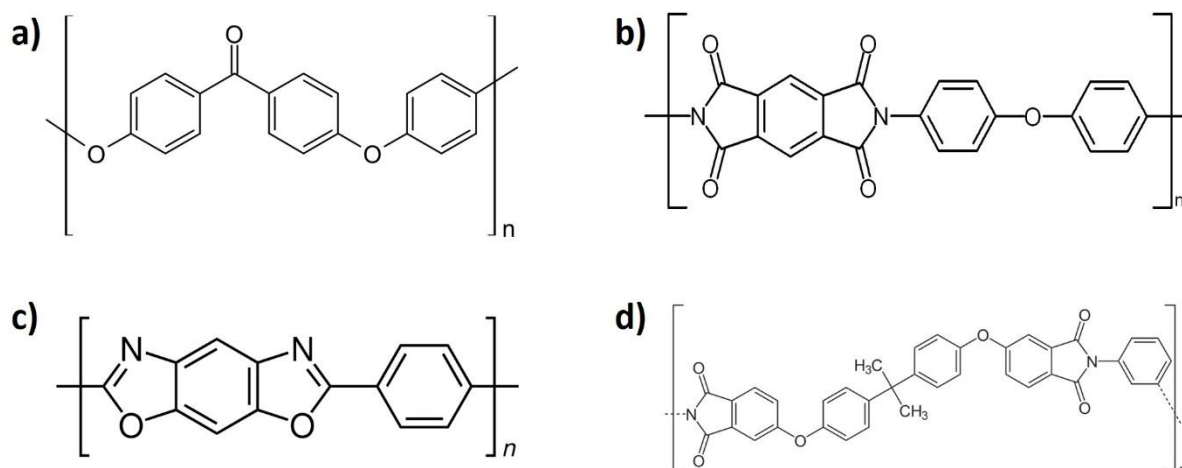


Figure 2. Structures of a) PolyEtherEtherKetone (PEEK), b) an example of PolyImide (PI) commercialized under the name "Kapton", c) PolyBenzOxazole (PBO), commercialized under the name Zylon and d) an example of PolyEther Imide (poly(bisphénol A-co-4-anhydride nitrophthalique-co-1,3-phénylènediamine)).

Another approach consists in modifying already-existing polymers by grafting active functions on the polymer backbone or by modifying the monomer with potentially fire-active functions before polymerization. Functions containing P, S, N, B, Si or other compounds have been grafted on various polymers to limit their flammability.[4] For example, phosphorus groups have been added to polyamide[5] or polystyrene[6] chains to produce fire retardant polymers. Because of its complexity, high costs, and often processing difficulty of the resulting materials, this method is usually restricted to highly technical applications.

The second method consists in incorporating fire retardant (FR) additives into the polymer matrix. This is the most commercially used method as processing is easy and low-cost. Problems to care for are the compatibility of fillers with the matrix. Also, high loadings are sometimes required, which can impact the mechanical properties of the polymer. Nevertheless, many systems have proven to be efficient. Chemistry of the fire retardant molecule or system is what drives its performance. Traditional FRs rely on chlorinated or brominated components, for example Tetrabromobisphenol A or hexabromocyclododecane.[7] They act mainly in the gas phase by inhibiting the radical reactions during the combustion. However, they are under scrutiny because of their suspected toxicity.[8] Due to their small size, they tend to migrate out of the polymer matrix and pollute the environment or cause risks to human health. A solution to this problem was the development of brominated and chlorinated polymers. But, in addition, the corrosive gases emitted during a fire still raise health and environmental concern. Despite their high efficiency, they are therefore being replaced by other solutions. Organophosphorus compounds have shown their effectiveness, especially when combined with other elements such as nitrogen. They limit fuel output by enhancing char forming ability leading to thermally stable residues. They can also act in the gas phase by poisoning combustion reactions. Nitrogen fire retardants act mainly in the gas phase by releasing nonflammable NH_3 gas and diluting the active species in the flame. However, they are mostly used as synergists in combination with other fire retardants, as their effect is limited. Metal hydroxides and carbonates have also been proven to be efficient, but only at high loadings, which usually modify the mechanical properties of the final material. For example, $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ act by decomposing and releasing H_2O . This endothermic reaction cools the material and the release of H_2O smothers the flame. They also act in condensed phase by forming a ceramic barrier. Then, mineral fillers such as talc, silicon, silicon oxides, boron compounds or transition metal oxides have shown interesting fire retardant (char formation enhancement, catalysis of char formation, synergists, formation of ceramic barriers...) and smoke-suppressing properties.[8] Nanocomposites are

also a class of materials having good fire properties, and have been studied a lot since their discovery. They act by forming a protective mineral layer upon heat exposure, acting as heat and mass transfer barrier.

Interesting fire performances are seen with intumescent systems (from the latin word *intumescere*, “to swell up”). Intumescent materials are composed of an acid source, a blowing agent and a carbon source. Upon heat exposure, the acid source decomposes and reacts with the carbon source to form a stable viscous cross-linked carbonaceous material. The blowing agent decomposes by releasing gases which will be trapped in the char and form an insulating carbon foam which protects the underlying polymer. The formulation can include nano- and/or micro-fillers as synergists (e.g. zeolites and clays). They either help the char formation or strengthen it to avoid the formation of cracks due to internal and external stresses.[9]

Intumescent systems have also been used as coatings, which is the last possible method to protect a polymer against fire. Although it also has some drawbacks (adhesion and durability being the main ones), adding a protective coating has several advantages when compared to the other two methods. First, the FR properties are concentrated at the surface, where the fire hits first, and there is less compatibility issues with the matrix. Finally, the functional properties of the materials are not or barely impacted. On a more fundamental point of view, it allows to act directly as a barrier against the mass and heat transfer driving the combustion process.[4]

In this work, the use of thin coatings has been investigated. Coatings with very low thicknesses have attracted a lot of the attention, mainly because they allow using a minimal amount of materials while still providing an efficient protection. Plasma, sol-gel, and others have been conducted to make thin coatings for many applications, including fire protection, with great success. [10], [11]

3. Sol-gel synthesis of fire protective thin coatings

The sol-gel process was introduced several decades ago and has been extensively studied ever since. It has focused a lot of interest, especially because it is carried out in soft conditions (low temperature, ambient pressure...) and because the processing of materials (particles, coating or monolith) is relatively easy. The process can be divided in three steps (see Figure 3). First, metal alkoxides $M(OR)_z$ (where M is a metal and R an alkyl group) are dispersed in a solvent to form a stable suspension of colloidal particles called a sol. Second, the metal alkoxides are

hydrolyzed. This step is catalyzed by an acid or a base. Afterwards, it is followed by a condensation step.

The resulted product is a vitreous network (the gel). Its composition depends on the reaction conditions and on the nature of metallic precursors. Hybrid organic-inorganic coatings can be produced depending on their chemistry. Usually silicon alkoxides such as tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) are used as precursors to give silica-like structures, but other metal alkoxides from Al, Ti etc. can be used, which gives access to a wide range of properties.[12]–[14]

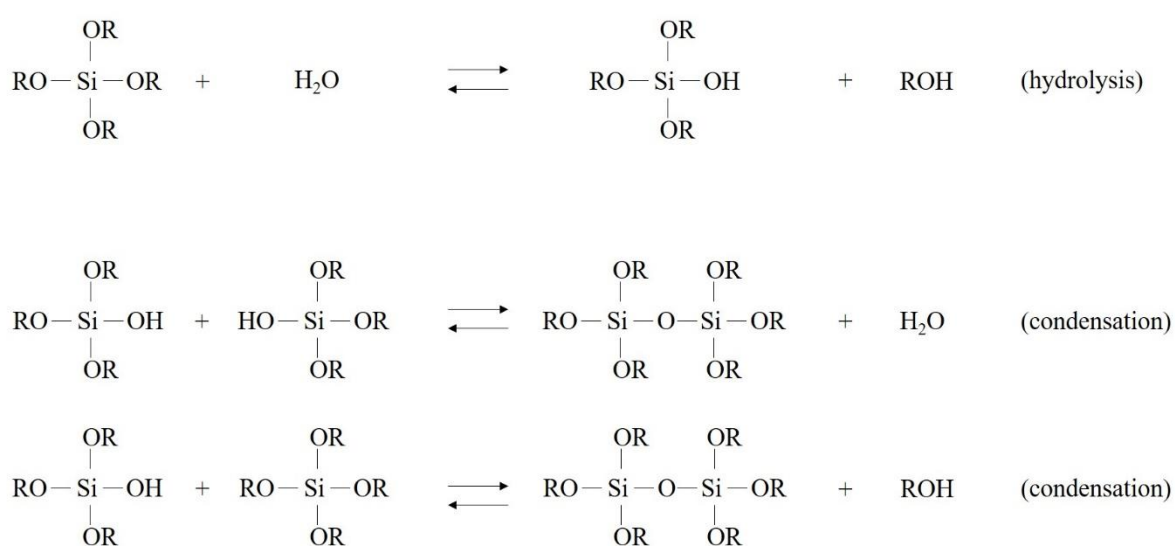


Figure 3. Sol-gel process. (example of silicon alkoxides)

Once dried, monoliths are usually fragile and broken down in powders, but thin functional sol-gel coatings have been developed throughout the years for various applications, including fire protection. First, sol-gel network can be used as additives in fire retardant coating formulations. They have been included in UV-curable resins for coatings which show potential for fire retardant applications.[15]–[21] They can also be casted as thin coatings on various substrates. They are applied either by dip-coating, spin coating, or by simply letting the water of a pool of gel evaporate.

The first records of sol-gel treatments for fire protection showed the potential of the approach for reducing the flammability of combustible materials. A coating of TEOS or a γ -

triethoxysilane terminated poly(1-caprolactone) was deposited on poly(methyl methacrylate) (PMMA) and increased the time to ignition by 55 % in a glow wire test. The protective effect was attributed to the accumulation of SiO₂ particles on the surface upon burning.[22] Additionally, a hybrid coating of poly(metacrylic acid), TEOS and perfluoroalkyltriethoxysilane on nylon carpeting gave good results in a pill test.[23]

Most sol-gel thin coatings for fire protection are applied on cotton fabrics, even if some studies mention their interest for Polyurethane foam (PUF) substrates,[24] expanded polystyrene (PS) foam,[25] polycarbonate (PC) panels[26] or wood.[27] All studies report either self-extinguishment, increase in limited oxygen index (LOI), or decrease in peak of heat release rate (pHRR), total heat release (THR) and total smoke release (TSR), depending on the tests performed. They also report the necessary synergism with other flame retardants such as phosphorus-based compounds.

Indeed, studies reporting the coating of polymers with silicon alkoxides only show either limited decrease of their flammability [28]–[30] or worsened combustion behavior, even if the time-to-ignition is sometimes longer.[31] Even if they don't provide significant protection, a silica coating can still enhance the charring of cotton when a small flame is applied,[32]–[36] and reduce its pHRR significantly (up to 35 %).[37], [38] On synthetic fabrics such as PET and PA66, a silica coating can prevent melt-dripping, which is a huge fire hazard,[39], [40] but also enhance the durability of other surface flame retardant treatments.[41]

As a matter of fact, the fire protective properties of sol-gel coatings are usually enhanced by taking advantage of the synergism existing between silicon and other compounds, by adding fire retardants in the sol formulation, or both. For example, interesting fire behavior was obtained by using phosphorus-doped sol-gel precursors, especially for cotton. Using diethylphosphatoethyltriethoxysilane (DPTES), for instance, enhanced the charring of cotton in a vertical fire test and reduced the pHRR and the TSR respectively by 52 and 56 % at cone calorimeter test.[42], [43] It was found that if the effect of silica was more prominent against a small flame, the synergism with P was necessary to improve the combustion behavior in a radiative scenario.[44], [45] Other strategies to use P and Si synergism is to treat the cotton by phosphorylation [34] or phenylphosphonic acid padding.[36] More commonly, phosphorous-containing molecules are added in the sol, such as aluminum phosphinate,[46], [47] phytic acid,[48]–[50] diethylphosphite,[33] ammonium polyphosphate,[51], [52] ammonium hexametaphosphate,[53] phenylphosphonic dichloride,[54] triphenylphosphate [55] or 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO).[56] The combination reduces the

pHRR and THR in MLC and brings self-extinguishment behavior, which can be further enhanced by the addition of a molecule containing nitrogen, in order to obtain a P-Si-N synergism.[33], [34], [47], [49], [57] For example, DPTES on cotton mixed with monoethanolamine rises the LOI of the fabric up to 29 %.[58] Phosphoramidate siloxane (DTSP) on cotton increases the LOI up to 30 %. The coatings enhance char formation, leading to self-extinguishment behavior in a vertical flame test (VFT), while the pHRR and THR are reduced by 68 % and 49 % respectively at mass loss calorimeter test (MLC).[59] Other flame retardants such as alumina particles [60] ZnO, [61] boric acid, borax, or boron-containing additives [55], [62], [63] have also successfully been used to bring self-extinguishment to the fabrics.

Sol-gel treatments have also shown promising effects on synthetic fibers. PA66 fabrics grafted with a phosphorylated chitosan and coated with a sol-gel coating of (3-aminopropyl) triethoxysilane (APTES) stopped the melt-dripping against a small flame and reduced the pHRR by 30 %.[39] Thanks to enhanced charring, the melt-dripping of PA6 fibers was also suppressed thanks to a TEOS sol-gel coating doped with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-modified vinyl trialkoxysilane (DOPOeVTS).[64] The synergism between P, N and Si in a sol-gel methyltrimethoxysilane (MTMS) coating containing urea and phosphoric acid also suppressed the melt-dripping of PET and raised its LOI up to 28 %.[65]

4. Plasma-aided formation of fire protective thin coatings

Plasma is a gas containing neutral species (atoms, molecules) and ions, either in their fundamental state or in an excited state, which emit electrons and photons during their de-excitation. It can be used to functionalize the surface of materials, either as a pre-treatment to enhance the adhesion of a coating or a finish, to induce the polymerization of active species, or to deposit functional molecules. Cold plasma in particular has gained interest as it avoids using thermal treatment or extensive amount of solvents. The development of atmospheric plasma also allows to get rid of expensive vacuum equipment.

Plasma pre-treatment of flammable substrates has been mainly used to graft and polymerize fire retardant molecules on textiles. Plasma polymerization of phosphate-containing monomers was first carried out by Akovali et al. on polyacrylonitrile (PAN) and PET fabrics. While keeping the thickness of the added layer below 10 μm , they observed an increase in LOI and a slight decrease of the burning rate of the fabrics. However, they state that the fire-retardant

species added must be efficient at small intake, otherwise the detrimental effect of the cross-linking of the fibers induced by plasma treatment would predominate. Plasma-induced polymerization of monomers containing phosphorus and/or silicon is privileged. Silicon or organophosphorus silicon monomers such as 1,1,3,3-tetramethyldisiloxane have been polymerized via plasma-assisted grafting on PA6 or PA6 powders, which increased the LOI by a few percent and reduced the pHRR and the THR respectively by 30 and 26 % at mass loss cone test.[66]–[69] Diethylphosphatoethyltriethoxysilane (DEPETS)[70] or hexamethyldisiloxane (HMDSO)[71] have been deposited respectively on PA6 and PC, and PA66 substrates. While with DEPETS the TTI was increased by 143 %, HMDSO reduced the TTI and decreased the pHRR by 30 % in mass loss cone calorimetry, without any change in THR and mass loss. However, the performance of silicon coatings can be improved by adding phosphorus molecules, for example triethylphosphate (TEP) with HMDSO on PC or PA6,[72] or vinyl phosphonic acid with cyclotetrasiloxane on cotton fabric.[73] The enhancement of the performance is believed to be due to condensed phase reactions as well as to a synergism between P and Si. A protective char layer is formed as a result, which helps reducing the pHRR and increasing the LOI considerably. But the particular interest of plasma-deposited fire retardant coatings is that they can enhance the performance of fire retardant substrates. For example, the fire performances of Proban and Nomex (commercial fire retardant fabrics) in a flash fire scenario were enhanced with a plasma-deposited HMDSO film.[74] The plasma-grafting of 1,1,3,3-tetramethyldisiloxane coating increased the LOI of PA6 nanocomposite from 22 % to 42 % and decreased the pHRR and THR by 41 % and 33 % respectively.[75] Several other studies are focused on the grafting of phosphate or phosphonate-functionalized acrylate monomers on PAN fabrics,[76] cotton,[77] silk,[78], [79] or polyethylene substrates.[80] The grafting of fire retardant precursors has also been carried out on Polyurethane Foam (PUF) substrates. A durable diethylvinylphosphonate coating, cross-linked with 1,4 butanedioldiacrylate, prevented melt-dripping and gave self-extinguishment behavior to the PUF substrates. Boron and fluorine chemistries have also been tested on PP[81] and PA6 [82] respectively.

Plasma treatment has also been used as a pre-treatment to enhance the adhesion of fire retardant molecules or coatings. A coating of montmorillonite platelets adsorbed thanks to the oxygen and radical species generated through plasma treatment increased the time to ignition of PET fabrics significantly.[83] Adhesion of organo-clay following the same principle (with an additional cross-linking step) decreased the pHRR of glass fibers reinforced epoxy

composites.[84] The same principle was applied for the padding of polyester fabrics with alkyl-phosphonate, which allowed the LOI to reach values superior to 30 %.[85] Additionally, a plasma-deposited coating of HDMSO also enhanced the adhesion of SiO₂ particles on PP and PS substrates.[86] Plasma treatments were also applied as post-treatment to increase the charring capacity and the durability of a coating via cross-linking.[87], [88]

5. Layer-by-layer coatings for fire protection

Despite the interest of sol-gel and plasma approaches in bringing fire retardant properties to different materials, the most extensively studied method to make flame retardant materials via a surface treatment is by applying a layer-by-layer coating. Indeed, a layer-by-layer surface treatment has proven to be a very efficient, versatile and facile strategy for the fire protection of various substrates. These coatings are very interesting as their protective effect is high, even if the thickness of the coating is below 1 μm . Therefore, they are discussed in more details in the next paragraph.

5.1 Generalities on nanocoatings made via layer-by-layer

Coatings made by layer-by-layer (LbL) have attracted a lot of interest since the technique was introduced in 1992 by Decher [89], [90] to improve the Langmuir-Blodgett technic and perfecting the work from Iler.[91] Layer-by-layer is a bottom-up nanofabrication technique for coatings or self-standing ultra-thin films (up to a few hundred micrometers). As opposed to the top-down method which relies on precise shaping of macroscopic materials into nanostructures, it uses physico-chemical processes to assemble elementary building blocks (polymers, nanoparticles, etc.) into macroscopic nanopatterned objects. Supramolecular chemistry is a famous example of a bottom-up method leading to complex structures by the self-assembly of molecules,[92] and despite it not being the original inspiration, some authors pointed out how similar this technic is to biological systems.[93], [94] The advantages of layer-by-layer in constructing thin films are multiple. First, it is an environmental-friendly process, as it is usually carried out in water. Then, it can be adapted to a wide range of substrates with complex structures, and it uses very little materials. The varieties of building blocks that can be used have also expanded the use of layer-by-layer coatings to many applications based on surface modification. The process relies on the self-assembly of two compounds driven by attractive forces. Commonly, electrostatic attraction between two compounds with opposite charges is what binds the layers together, but it was expanded to hydrogen bonding, covalent bonding,

van der Waals forces, complexes formation... Basically, any type of acceptor/donor interactions. This results in coatings with controllable thickness and structures.

Using electrostatic interactions as an example, a charged substrate is immersed in a solution of ionic species of the opposite charge. At the surface, these are attracted by the substrate and form ionic complexes. Any excess or weakly adsorbed ions are rinsed by dipping the substrate in water, before immersing it once again (with an optional drying step) in a solution of ions of opposite charge, and rinsing it. This process creates a bilayer, and is repeated the necessary number of times to reach the required bilayer number or the required thickness. This is usually controlled by Quartz Crystal Microbalance (QCM) on silicon wafers, or by UV-Visible spectroscopy. The process is illustrated in Figure 4.

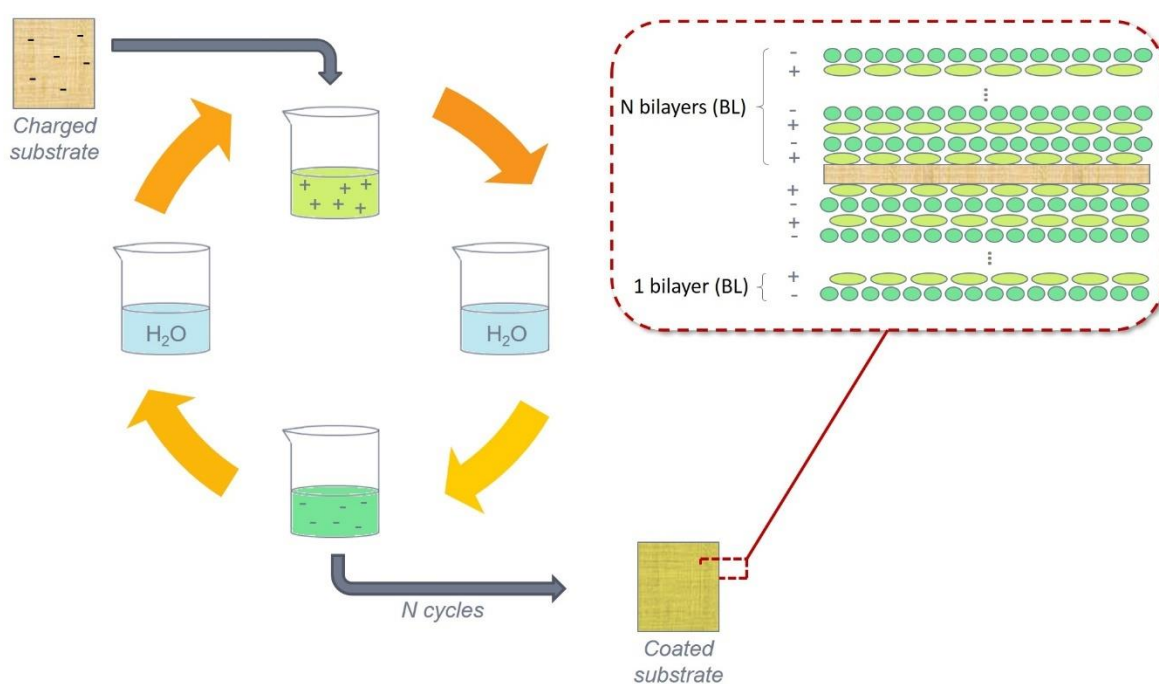


Figure 4. Schematic illustration of the layer-by-layer process (example of electrostatic interaction, with a negatively charged substrate).

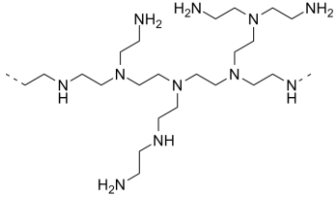
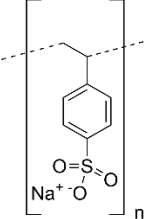
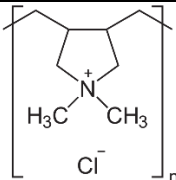
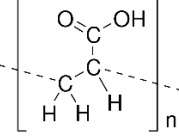
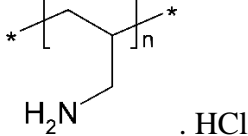
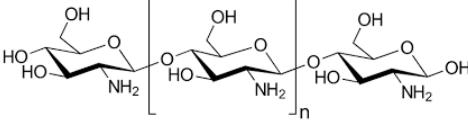
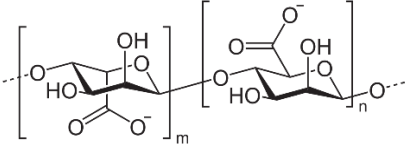
The coating grows from the surface, and the growth profile depends on a lot of parameters. The charge density is important for instance, as well as the ionic force of the solution or the nature of the salt, which can induce more or less screening of the charge, and can cause coiling of polymers' chain, for example. Other parameters can influence the film's growth and morphology, such as the characteristics of the surface (charge density, roughness...),

characteristics of the solution (concentration, pH, presence, nature and concentration of added salts...), or deposition conditions (time of adsorption, dipping speed, stirring, temperature, humidity of the environment, drying conditions, rinsing...).[90], [95] There are two growth profiles: linear and exponential. Linear growth happens when there is no diffusion at the interface. In that case, the deposition of a layer depends on its charge and on the charge of the surface, resulting in a thickness proportional to the number of layers. Exponential growth happens when there is diffusion at the interface. It is sometimes sought after because it means a higher thickness can be reached after fewer numbers of steps. First it was believed that the formation of coacervates, with a roughness increasing with the thickness, was responsible for this phenomenon, or a swelling and increased water absorption. However, it was proven that polycation diffusion in and out of the film was the cause.[96] Polycations diffuse in the film during cationic deposition, but out of the film during the rinsing steps and the polyanions deposition. There they form a complex with the incoming anions. Thickness was found to be proportional to the number of cations diffusing out of the coating.[97]

Layer-by-layer thin coatings can be built by a variety of techniques, including dip-coating, [98]–[105] spin-coating [106]–[111], spray coating [112], [113], roll-to-roll processes [114], [115]... depending on the scale, available instrumentation and substrate. For example, dip-coating is usually the preferred method for complex substrates such as foam or textiles, while roll-to-roll is adapted from textile finishing techniques; spin and spray-coating are usually used for flat surfaces. Automatic instrumentation and innovative processes are sought in order to reduce the deposition time and efforts. For example, Gittleson et al. conceived an automated spin-spray instrumentation,[116] Seo et al. an automatic spraying system,[117] while Prof Grunlan's group developed a continuous automatic dip-coating method for textile[118] as well as for various substrates[114]. Carosio et al. relied on padding to create efficient fire retardant layer-by-layer coatings on polyurethane foams within a matter of seconds[119].

As it was mentioned above, LbL allows for using a large variety of building blocks, from polymers to colloids or surfactants. PolyEthyleneImine (PEI), sodium Poly(Styrene Sulfonate) (Na-PSS), Poly(diallyldimethylammonium chloride) (PDADMAC), Poly (Acrylic Acid) (PAA), Poly(Allylamine Hydrochloride) (PAH) as polymer electrolytes have been used extensively since they can have high density charged according to pH. Biopolymers such as polysaccharides (chitosan, alginate...) have also been studied in layer-by-layer process because of their ionic nature (Table 1).

Table 1. Examples of polymers, synthetic and biobased commonly used in layer-by-layer processes

Type	Formula	Name
Synthetic polymers		Branched Polyethyleneimine (BPEI)
		Sodium Poly(Styrene Sulfonate) (Na-PSS)
		Poly(diallyldimethylammonium chloride) (PDADMAC)
		Poly (Acrylic Acid) (PAA)
		Poly(Allylamine Hydrochloride) (PAH)
Biosourced polymers		Chitosan
		Alginate

Polyelectrolytes multilayer films as well as composite coatings have been fabricated by this method using an extensive amount of different nanoparticles, from silicon-based nanoparticles such as Polyhedral Oligomeric Silsesquioxane (POSS),[120]–[122] SiO₂ [123]–[125] to carbon-based nanoparticles and other inorganic species depending on the application and trends. In that case, polymers play the role of a binder between inorganic particles, even if some papers report the design of all-inorganic coatings.[126]

5.2 Using layer-by-layer coating strategies for the fire protection of flammable substrates

Fire protection of flammable substrates by layer-by-layer coatings has been quite developed for a couple of decades. As mentioned in the paper by Holder et al.,[127] the first suggestion of using layer-by-layer coatings was made by Srikulkit et al. in 2006.[128] Despite the fact that they made no fire test, they demonstrated the interest of using such coatings for this purpose. 10 to 60 bilayers of Chitosan and Polyphosphoric acid were deposited on silk, and thermogravimetric analysis (TGA) at 10°C/min in air showed a delayed degradation starting from 30 bilayers as well as an increased residual mass. In 2009, Li et al. demonstrated their interest again by depositing 10 bilayers of branched polyethyleneimine (BPEI) and Laponite (LAP) on cotton fabrics and testing them with a vertical flame test. The idea was to mimic the behavior of flame retardant composites. During fire tests, the clay fillers tend to migrate to the exposed surface and form a protective ceramic barrier. Therefore, by forming the barrier from the get-go, the coating should protect the underlying substrate as it does for composite materials. In this study, the samples combusted completely but had a higher charring capacity, which increased with the thickness of the coating, here monitored by the pH of the laponite solution.[129] They then tested the same system by replacing laponite particles with montmorillonite platelets and obtained similar results. Quantitative results were given from a Microscale Combustion Calorimetry (MCC) test that showed a decrease in the Heat Release capacity (HRC) and in the Total Heat Release (THR).[130]

Table 2. First Layer-by-layer fire protective coatings

Substrat	Material	System	Number of bilayers	Result	Reference
Textile	Silk	Chitosan/Phosphoric acid	30 to 60	TGA : delayed degradation	[128]
Textile	Cotton	BPEI/Laponite	10	VFT: complete combustion but higher charring capacity	[129]
Textile	Cotton	BPEI/Montmorillonite	10	VFT: complete combustion but higher charring capacity MCC: THR -20 %; HRC-15 %	[130]

From then on, the number of articles published on the subject has grown up exponentially. The fact that impressive fire protective performances could be reached with only a few dozens of nanometers initiated lots of research. Most works focus on textile and polyurethane foam substrates, but some works have been done on polymer sheets or films. Different approaches

are pursued. First, coatings consisting of polyelectrolytes multilayers have been extensively developed in an all-polymer approach, usually relying on intumescent mechanisms. Strict composite coatings as passive barriers have also been designed, as well as layer-by-layer systems based on a combination of both.[11]

5.2.1 All-polymer layer-by-layer fire protective coatings

5.2.1.1 *Intumescent Polyelectrolytes*

The first example of intumescent polyelectrolyte complex consisted in 20 bilayers of Poly(sodium Phosphate) (PSP) in combination with Poly(allylamine) (PAH), tested on a cotton substrate which acts as the carbon source. It showed great reduction in peak of heat release rate (-63 %) and THR (-68 %) using micro calorimetry, and quick extinction during the cone calorimeter test (reduction of 43 % and 51 % of the pHRR and THR respectively).[131] On PolyLactic Acid (PLA) sheets, the same system but reinforced with montmorillonite particles showed similar results using cone calorimetry.[132] It was then deposited on PA66 fabrics, which also improved their fire retardancy, however with less exciting results (reduction by 36 % of pHRR) due to the coating not penetrating in between the fibers.[133] The addition of TiO₂ particles did not improve the performance.[134] On Polyester cotton blends, it was deposited as a polyelectrolyte complex in a one-pot process, which improved their flame retardant behavior (attributed to a higher nitrogen content) and their washing durability.[135] Their effectiveness, coupled with low weight gain, low thickness and the facile procedure, spurred on a lot of research. The scientific community strived to find new systems, that are either more efficient, that grow thicker or give equal to better results with a fewer number of layers, or that use renewable or bio-based resources. For example, cottons have been covered with 30 bilayers of chitosan (CH) and phytic acid (PA), showing great results for systems with the highest phosphorus content (pHRR and THR reduced by 60 % and 76 % respectively during cone calorimetry, and self-extinguishment during vertical fire test).[136] Pan et al. then added sulfonated melamine-formaldehyde to the phytic acid solution as a blowing agent, this system achieving self-extinguishment with only 10 bilayers.[137] The same system was deposited using layer-by-layer technology on PA66 fabrics, followed by borate cross-linking [138] or in combination with oxidized sodium alginate,[139] as well as on wool fabric in a one pot procedure as a polyelectrolyte complex, along with citric acid to increase durability.[140] Flammability of both systems was successfully decreased. Kundu et al. reported a 26 % decrease in pHRR from mass loss cone experiments, with an increased LOI and a V-1 rating at

UL94 test, while Cheng et al. reported a 39 % pHRR reduction during microcalorimeter measurements, coupled with a decrease in THR, smoke density and an increased char yield.

Other examples of intumescent LbL coatings on textile have been carried out with different systems, researchers trying to find the most efficient one. Cotton is by far the most studied substrate, because of its high flammability and its extensive industrial use, however synthetic fibers (PA66 and Polyester fabrics) and natural fibers (Ramie) were also effectively protected by intumescent systems.

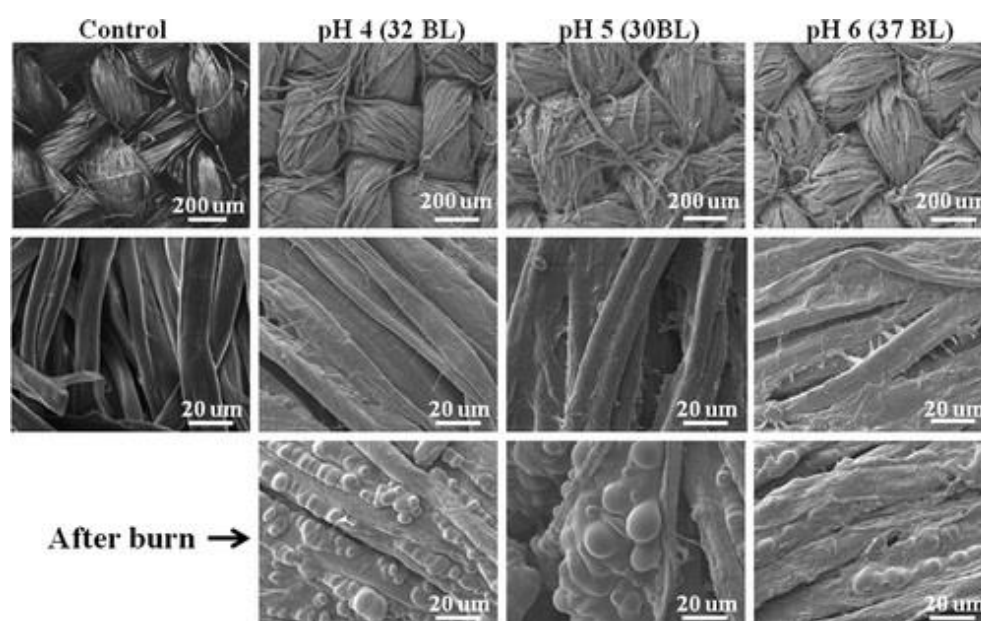


Figure 5. SEM images of coated and uncoated cotton fabric before (top two rows) and after (bottom row) vertical burn testing. The uncoated fabric was completely consumed during burning, so no postburn image can be shown.

Reprinted (adapted) with permission from G. Laufer et al., "Intumescent multilayer nanocoating, made with renewable polyelectrolytes, for flame-retardant cotton," *Biomacromolecules*, vol. 13, no. 9, pp. 2843–2848, 2012, doi: 10.1021/bm300873b. Copyright © 2012, American Chemical Society [136]

With the constant concern of trying to find environmentally benign systems, bio-based materials are almost constantly used, with ionic chitosan being a major component used as a carbon source, and sometimes as both a carbon source and blowing agent, given by the presence of amino groups. It has been used in intumescent polyelectrolyte layer-by-layer assemblies in association with ammonium polyphosphate (APP) on cotton,[141], [142] polyester-cotton blends[143] and polyester fabrics (where the combination with guanidine sulfamate, urea and thiourea showed better flame retardancy, with fewer bilayers [144]) or with PU latex.[145] It

was also combined with Poly(sodium Phosphate) [118], [146] (the addition of amine salts in the rinsing water thickens the coating and helps achieving good flame retardancy with fewer bilayers [147]), with phosphorylated chitin on cotton,[148] with phosphorylated chitosan on PA66,[149] or even with DNA on cotton [150] for fully renewable flame retardant coatings. Hypophosphorus acid-modified chitosan was deposited along with Polyethylenimine and genipin cross-linking which achieved self-extinguishment in horizontal flame test and a reduction of 73 % and 80 % of the pHRR and THR respectively in micro scale combustion calorimeter [151] (also on polyester-cotton blends, without genipin as cross-linker, and with similar vertical flame test results [152]). In addition to the previously-mentioned chitosan-phytic acid systems, phytic acid was used in combination with a sol-gel synthesized nitrogen modified silane on cotton,[153] with PEI and Melamine on cotton (pHRR reduced by 50 % in MLC tests with an additional PDMS hydrophobic treatment [154]), and with polysiloxane on polyester fabric where it suppressed the dripping phenomenon, enhanced charring and reduced pHRR in MCC tests.[155] Then, Fang et al. focused on using polyhexamethylene guanidine phosphate (PHMGP) in a layer-by-layer intumescent assembly on cotton with potassium alginate,[156] Sodium Polyborate [157] and APP.[158] APP being a classic acid-source in intumescent systems, it was also extensively used, with BPEI on cotton[159] and on Ramie fabric [160],[161], or with Poly(Acrylic Acid) and Poly(diallyldimethylammonium chloride) (PDADMAC) on cotton, polyester-cotton blend and polyester fabric,[162] for example. An original layer-by-layer system consisting in phosphonated oligoallylamines et oligoallylamines on cotton was also studied by Carosio et al.[163] NH₂-rich polysiloxanes with APP also gave good results in protecting Nylon-Cotton blends for military application, showing the versatility of the system and its large potential area of application.[164]

Table 3. Intumescent layer-by-layer coating on textile

Material	System	Number of units	Result	Reference
Cotton	PSP/PAH	20	MCC: pHRR-63%; THR-68% MLC: pHRR-43%; THR-51%	[131]
Cotton	CH/PA	30	VFT: self-extinguishment MLC: pHRR-60%; THR-76%	[136]
Cotton	CH/(PA+sulfonated melamine formaldehyde)	10	VFT: self-extinguishment	[137]
Cotton	CH/APP	20	MCC: pHRR-80%; THR-82% VFT: enhanced charring, reduced burning time	[141], [142]
Cotton	CH/APP+UV-curable PU	3	LOI: 25% VFT: self-extinguishment MLC: pHRR-11%; THR-32%	[145]

Cotton	CH/PSP	30	VFT: self-extinguishment	[118]
Cotton	CH/PSP+sonication	17	VFT: Self-extinguishment MCC: pHRR-73%; THR-81%	[146]
Cotton	CH/PSP + amine salt treatment	10	VFT: self-extinguishment MCC: pHRR-73%; THR-78%	[147]
Cotton	CH/phosphorylated chitin	20	VFT: self-extinguishment MCC: pHRR-74%; THR-86%	[148]
Cotton	CH/DNA	20	VFT: self-extinguishment LOI: 24% MLC: pHRR-40%	[150]
Cotton	Hypophosphoric acid-modified CH/PEI	10	HFT: self-extinguishment MCC: pHRR-73%; THR-80%	[151]
Cotton	N-modified silane/PA	15	VFT: self-extinguishment MLC: pHRR-31%; THR-38%	[153]
Cotton	PEI+Melamine/PA	4	VFT: self-extinguishment MLC: pHRR-59%; THR-24%	[154]
Cotton	Potassium alginate/PHMGP	20	VFT: enhanced charring MCC: pHRR-29%; THR-24%	[156]
Cotton	Sodium polyborate/PHMGP	10	VFT: self-extinguishment LOI: 29% (20BL: 41%) MCC: pHRR-78%; THR-69%	[157]
Cotton	APP/PHMGP	10	VFT: enhanced charring	[158]
Cotton	APP/BPEI	PEC	HFT: self-extinguishment MLC pHRR-51%	[159]
Cotton	phosphonated oligoallylamines and oligoallylamines	5	VFT: enhanced charring and no afterglow	[163]
Cotton, PET, PET- Cotton	PDADMAC/PAA/PDADMAC/ APP	10	HFT: self-extinguishment VFT: enhanced charring MLC: reduced pHRR and THR for all substrates and for 25,35 and 50 kW/m ²	[162]
PET-cotton	Hypophosphorous acid-modified CH/BPEI	20	HFT: self-extinguishment	[152]
PET-Cotton	CH/APP	20	VFT: no afterglow, enhanced charring MLC: pHRR-24%; THR-22%	[143]
Nylon- cotton	NH ₂ -rich polysiloxanes/APP	20	VFT: self-extinguishment	[164]
Ramie	PEI/APP	20 (dip- coating)	VFT: self-extinguishment MCC: pHRR-65%; THR-68% MLC: pHRR-42%; THR-25%	[160]
		20 (spray- coating)	VFT: self-extinguishment MCC: pHRR-74%; THR-60% MLC: pHRR-54%; THR-60%	[161]
Wool	CH/PA, citric acid crosslinking	PEC	MCC: pHRR-39; THR-41; reduction of smoke density	[140]
PA66	CH/PA+ borate cross-linking	10	LOI up to 21.5% MLC: pHRR-26% UL94: V1 rating	[138]
PA66	CH/PA/CH/oxidized alginate	5, 10, 15	5QL: MLC: pHRR-24% 10 and 15OL: VFT: suppressed melt-dripping LOI 21-22%	[139]

PA66	PSP/PAH	40	MLC: pHRR-60%	[133]
PA66	CH/phosphorylated CH+polyacrylate de sodium	10	LOI: 23% MLC: pHRR-25% UL94: V1 rating	[149]
PA6	PAH-PSP-PAH-TiO ₂	15	MLC: pHRR-26%	[134]
PET			No effect in MLC	
PET	CH/APP with N or N and S based derivatives	10	MLC: pHRR-61.7% LOI 26% VFT: self-extinguishment	[144]
PET	Polysiloxane/PA	1,5	VFT: enhanced charring, reduced burning rate MLC: pHRR-65%;THR-59%;TSR-72% LOI 31.4	[155]

With the already mentioned exception of the work by Laachachi et al. on PLA films,[132] it seems that most intumescent all-polymer coatings have been deposited on textile fabrics. However, some works were also performed on PET, silicon and PU foams with relatively good results. APP combined with PDADMAC and PAA managed to suppress the melt-dripping of the PET foam and to reduce the pHRR by 25 % at MLC tests.[165] Combined with Chitosan on silicon foam, it decreased the pHRR and smoke release by 28 % and 42 % respectively.[166] On the PU foam, chitosan/phosphorylated cellulose as well as chitosan and poly(Phosphoric acid) suppressed melt-dripping and reduced the pHRR by around 30 %. [119], [167]

Paper is also a flammable material that needs protection and LbL strategies were developed for this substrate. Xuan et al. directly coated paper and obtained self-extinguishment using a host-guest layer-by-layer self-healing coating of poly (acrylic acid)-adamantanamine/ammonium polyphosphate-cross-poly (ethylenimine)- β -cyclodextrin (PAA-AD/APP-co-PEI- β -CD)).[168] Some researchers prefer to directly treat the fibers before assembling them in a paper sheet. Chitosan combined with poly(vinyl phosphonic acid) (PVP) was used in a 20 BL layer-by-layer treatment to coat wood fibers and make fire retardant paper, which reduced pHRR and THR by nearly half, and caused self-extinguishment in horizontal flame testing.[169] A high molecular weight PEI was found to adsorb more on the substrate and form a continuous coating with good coverage on cellulose fibers, which, combined with high quantity of sodium hexametaphosphate in a 3.5 BL coating, gave a self-extinguishing behavior to the paper.[170] Same behavior and also reduced HRR in MCC test was obtained with PEI and Melamine deposited along with phytic acid.[171]

Table 4. Intumescent layer-by-layer coatings on other substrates

Substrate	Material	System	Number of units	Result	Reference
Polymer sheet	PLA	Poly(allylamine)/MMT	30 and 60	MLC (30): TTI+60%, pHRR-8%; THR-22% MLC (60): TTI+96%; pHRR-36%; THR+6%	[132]
		Poly(allylamine)/MMT + PsP		MLC (30): TTI+96%, pHRR-13%; THR-6% MLC (60): TTI+111%; pHRR-37%; THR+0%	
Foam	PET	PAA/PDADMAC/APP or DNA/PDADMAC	4	HFT: no dripping, self-extinguishment MLC: with APP pHRR-25%	[165]
	Si	CH/APP	7	LOI 23.8% MLC: pHRR-28%; THR-15%; TSR -42%	[166]
	PU	CH/phosphorylated cellulose nanofibers	5	HFT: no melt dripping MLC: pHRR-31%	[167]
	PU	CH/poly(phosphoric acid)	2	MLC: pHRR-33%	[119]
Paper		PAA-adamantine/APP-co-PEI- β -cyclodextrin	15	Self-extinguishment against the flame of a lighter	[168]
Fibers for paper making	Wood pulp	CH/poly(vinylphosphoric acid)	20	HFT: self-extinguishment; MLC: pHRR-49%; THR-33%	[169]
	cellulose	High molecular weight-PEI/sodium hexametaphosphate	3.5	HFT: self-extinguishment VFT: enhanced charring LOI: 25%	[170]
	paper	PEI+Melamine/PA	8	MCC: pHRR-43%; THR-49	[171]

These intumescent coatings usually form a stable char, and high residual masses are observed after fire test. Self-extinguishment characterizes the most efficient systems, smoke reduction as well as pHRR and THR reduction from MCC or MLC tests are also reported. SEM observations of the char show the presence of microbubbles characteristic of intumescence, however the terms “intumescent-like” or “catalytic charring” are more cautiously used and seem to be more accurate. Indeed, the presence of phosphate groups in large amount seems to favor the formation of the protective char, by catalyzing its formation. Whole and coherent coverage of the fabric seems to be the key element between complete combustion with “just” enhanced charring, and self-extinguishment with actual pHRR, THR and smoke reduction. In the paper by Jimenez et al., the term “micro-intumescence” is used to describe the phenomenon. Its mechanism was investigated, and it was found that the presence of phosphate groups catalyzes the dehydration of chitosan and cellulose fibers, leading to the decomposition of the LbL coating and the formation of a thermally stable char. According to TGA results, this step occurs at a lower temperature than the decomposition of cellulose, which explains the shorter time to ignition observed in cone calorimetry. The char acts as a barrier against heat transfer, effectively protecting the substrate, and traps the combustible gases formed, which results in the observed

bubbles on the char. In addition, the dehydration step releases large quantities of water which extinguish the flame and cool the material. This explains the shorter burning time, as well as the enhanced charring and reduced HRR.[141]

5.2.1.2 Non intumescent systems

In parallel, some research pointed out that an intumescent mechanism is not always necessarily needed to impart fire protection. On textile, coatings of PEI and alginate cross-linked with metal ions on cotton also showed enhanced charring, although not sufficient enough to reach good fire protection.[172] PEI and oxidized alginate crosslinked with hypophosphorus acid could also protect PET fabric by suppressing melt-dripping and reducing pHRR during cone calorimetry.[173] Combinations, applied on cotton, of starch and polyphosphoric acid,[174] chitosan with melamine and Poly(sodium Phosphate),[175] or polysiloxane and phytic acid with PEI [176] caused self-extinguishment with only a few bilayers. In all these systems, the presence of a char stable enough is necessary to reach good fire protection. These kinds of systems were also applied to protect foams. On PU foam substrates, a pHRR reduction of 52 % was reached by taking advantage of the emission of large quantities of diluting gases (H_2O , SO_2 , NH_3 ...) from a Chitosan/Poly(vinyl sulfonic acid sodium) 10 BL layer-by-layer coating.[177] Following the same principle, a pHRR reduction of 42 % was reached with a Chitosan/Lignosulfonate 8BL coating.[178] Carosio et al chose to work with phosphorus filled coatings, with poly(phosphorus acid) or poly(allylamine diphosphonate) in association respectively with chitosan and polyacrylic acid assembled in quadlayers (QL),[179] or with chitosan only.[180] Both systems could sustain high heat fluxes with great HRR reduction (both showed a 55 % reduction in pHRR when exposed to a radiative 35 kW/m² heat flux). All systems helped maintaining the polyurethane open-cell shape by forming an exoskeleton during fire test.

Table 5. All polymer non-intumescent layer-by-layer fire protective coatings

Substrat	Material	System	Number of units	Result	Reference
Textile	Cotton	PEI/alginate+metal ion cross-linking	10	VFT: With Ba ion, enhanced charring and reduced burning rate	[172]
		Starch/Poly(phosphoric acid)	2	HFT: Self-extinguishment MLC: pHRR and THR reduced by about 50% depending on the density of the cotton	[174]
		N-containing polysiloxane	30	LOI: 30% VFT: self-extinguishment	[176]
	PET-Cotton	CH+Melamine/sodium hexametaphosphate	15	VFT: self-extinguishment MCC pHRR-29%; THR-37%	[175]
	Polyacrylamide-grafted PET	PEI/oxidized alginate + hypophosphorous acid crosslinking	15	HFT: self-extinguishment MLC: pHRR-44%; THR-22%	[173]
Foam	PU	CH/poly(vinyl sulfonic acid)	10	Torch test: stops flame spread MLC: pHRR-52%	[177]
		CH/lignosulfate	8	HFT: no melt-dripping MLC: pHRR-42%	[178]
		PAA/CH/poly(phosphoric acid)/CH	5	HFT: Self-extinguishment MLC: pHRR -50 to 60% depending on heat flux Burn-through torch test: temperature on back side kept under 100°C LOI: 23%	[179]
		CH/poly(allylamine diphosphonate)	2	HFT: no melt-dripping MLC: pHRR-48%	[180]

5.2.1.3 Other applications of Layer-by-layer all polymer coatings

The layer-by-layer coating technique was also employed, not to coat substrates, but to coat particles or fibers that would then be used either as filler or as composite reinforcement in a polymer matrix. These studies are usually carried out with LbL systems which have already been proven to be efficient in other studies on textile. For example, CH/lignosulfonate LbL system was used to coat hydroxyapatite to impart fire retardancy to PolyVinyl Alcohol (PVA) with very low loading.[181] Hollow mesoporous silica was coated with chitosan and phosphorylated chitosan in epoxy resin, reducing the pHRR by 51 % thanks to a higher char yield.[182] Yan et al prepared flame retardant ramie fabric through the deposition of poly(diphenolic acid-phenyl phosphate) and PEI, while Li et al chose APP and PEI, and included it in benzoxazine resin to prepare self-extinguishing laminates.[183]–[185] Layer-by-

layer coating technique was also used for the fire retardancy of carbon fiber/epoxy composite through the functionalization of carbon fibers with one bilayer of PEI and PAA.[186]

5.2.2 All inorganic layer-by-layer fire protective coatings

Coatings made with bilayers of SiO₂ and alumina-coated SiO₂ on PET fabrics showed a decrease in pHRR of 38 % for the best system, with no dripping and reduced burning and after-flame time. However, it was shown that only the coatings that managed to maintain a continuous coverage of the fabric could have an actual effect on the fire behavior.[187] This was achieved with horizontal spray layer-by-layer coating on cotton and PET fabric,[188], [189] which yielded a homogeneous and compact coverage of the fibers, highlighting the importance of the deposition technique. This led to a higher time to ignition, and lower pHRR, THR and smoke production. Similar results were obtained on PC sheets, where 20BL suppressed melt-dripping, lengthened the time to ignition, and reduced the HRR (the protection was however not enough for thicker PC substrates).[190] The only example of an all inorganic coating on foam that we are aware of was reported by Patra et al. and also relied on a clay sheets/metal-based particles combination. Vermiculite (VMT) platelets along with boehmite particles reduced pHRR and smoke release by around 50 % with only a single bilayer. The only default was the coating fragility, which cracked easily during the test, however, it was not that critical and it still created a protective layer by keeping the foam skeleton intact.[126]

Table 6. All-inorganic layer-by-layer fire protective coating.

Substrat	Material	System	Number of units	Result	Reference
Textile	PET	Cationic SiO ₂ /anionic SiO ₂ Dip coating	5	MLC: TTI+45%; pHRR -20% VFT: no melt-dripping	[187]
		Cationic SiO ₂ /anionic SiO ₂		MLC: TTI +21%; pHRR-34%; TSR-30%	[189]
	Cotton	Horizontal spray		MLC: TTI +27%; pHRR-20% VFT: increased residue	[188]
Polymer	0.2 mm PC	Cationic SiO ₂ /anionic SiO ₂	5	MLC: pHRR-20%; THR-30% VFT: no melt-dripping at 20BL	[190]
	1 mm PC			No improvement of flammability	
Foam	PU	Vermiculite/Boehmite	1	MLC: pHRR-55%; TSR-50%	[126]

5.2.3 Layer-by-layer composite coatings

5.2.3.1 Composite intumescent polyelectrolytes

The combination of intumescent layer-by-layer coating with nanoparticles has also been studied, with the idea of either providing an additional barrier, strengthening or reinforcing the char, or even catalyze its formation.

On textile, cotton substrates have been the most studied with the exception of one study on polyester-cotton blend [191], on PA66 and Polyester,[134] and two studies on ramie.[192], [193] Silicon-based particles such as clay [114], [194] or SiO₂ [103], [191], [195] have been used, as well as carbon based particle: graphene oxide (GO), single wall carbon nanotube (SWCNT) and multi wall carbon nanotubes (MWCNT).[196]–[199] α -ZrP sheets,[200] hydrotalcite particles [201] and TiO₂ particules [134] were also added in layer-by-layer coatings for fire protection. In some cases, the behavior was improved when compared to intumescent-only coatings, at two conditions. First, the presence of nanoparticle should not impart the intumescent properties of the coating [201] and then, there must be a good coverage.[134] Either previously mentioned systems were used, or intrinsically intumescent polymers were synthesized by grafting phosphorus-containing groups on the polymer backbone [194], [196].

Table 7. Composite intumescent layer-by-layer fire protective coating on textile.

Textile	System	Number of units	Result	Reference
Cotton	BPEI/APP+fluorinatedSiO ₂ /PDMS	1	MCC: pHRR-86%; THR: -39% VFT: self-extinguishment	[103]
	BPEI+urea+diammonium phosphate/Kaolin	50	MCC: pHRR-72%; THR: -79% VFT: self-extinguishment	[114]
	FR-PAA/MMT	20	MLC: TTI+40%; pHRR-46%; THR-18%	[194]
	PEI-SiO ₂ /Poly(phosphoric acid)	Not mentioned	LOI: 28.2% VFT: self-extinguishment	[195]
	FR-polyacrylamide/GO	20	MLC: TII+56%; pHRR-50%; THR-22%	[196]
	Phosphorylated GO/PEI	10	MLC: pHRR-27%; THR-21% VFT: cohesive residue	[197]
	Polyhexamethylene guanidine phosphate (PHMGP)/potassium alginate-CNT	20	VFT: cohesive residue, no afterglow	[198]
	PHMGP/modified MWCNT	20	MCC: pHRR-35%; THR-37% VFT: cohesive residue, no afterglow	[199]
	PHMGP/APP/PHMGP/ZrP	20	MCC: pHRR-59%; THR-53% VFT: cohesive residue, no afterglow	[200]
	PDADMAC/DNA+hydrotalcite post-diffusion	10	HFT: self-extinguishment MCC : pHRR-33%	[201]
Ramie	PEI/ZrP+PEI/APP	5+5	MCC: pHRR-53%; THR-56% VFT: cohesive residue	[192]
	Amino-MWCNT/APP	20	MCC: pHRR-36%; THR-25% VFT: cohesive residue	[193]
PET-cotton	Cationic SiO ₂ /anionic SiO ₂ /CH/APP	10	MLC: TTI: +37%; pHRR-11%; THR-22% VFT: no afterglow	[191]
PET	PAH/PSP/PAHTiO ₂	15	MCC: pHRR-14%	[134]
PA66			MCC: pHRR-26%	

On PUF substrates, the combination of inorganic particles yields great pHRR reduction from 39% for 2 Trilayer (TL) PEI/GO/Melanin nanoparticles [202] to 54 % for 4TL PAH/PSP/MMT [203] and 67% for 5QL/CH/APP/CH/PAA-stabilized Kaolin.[204] It has been attributed to the formation of thermally stable, coherent, graphitized [202] and swollen chars that form exoskeletons able to retain the foam's shape. 5 quadlayer (QL) CH/sodium hexametaphosphate/CH/silicon-based nanoparticles was also applied on cellulose fibers to create fire retardant paper. Montmorillonite (MMT) platelets, Sepiolite (SEP) and colloidal silica were used and tested by horizontal flame testing and MLC. All three maintained the fiber shape upon burning while cotton was combusted underneath. MMT and SEP showed self-extinguishing behavior by forming a compact char layer, and pHRR reductions of 44 and 47 % were observed, respectively. Smoke suppressing properties were obtained for SEP and SiO₂, though the low packing density of SiO₂ provoked worse fire behavior.[205] Combining a passive

organic/inorganic barrier with an intumescent coating is also another strategy, where the inorganic barrier delays the degradation to give time for the intumescent system to react to the thermal constraint. This was applied with a 20 BL CH/APP coating on top of a 4 BL CH/VMT barrier.[206] Also, the combination of a passive CH/MMT barrier with a PDADMAC/Boehmite layer (aiming at releasing water to dilute the flame and cooling the material) and an APP/MMT coating applied on top was tested.[207] Both systems reduced the pHRR by 50 % as well as smoke production during cone calorimetry, however the second made it with only 1 TL. The application of a composite intumescent system to coat an inflammable aerogel should also be mentioned because of the exceptional protection the total system can provide, with an 80 % reduction of pHRR during cone calorimetry. A cellulose nanofibrils aerogel was coated with a layer-by-layer coating made by CH, PVP and MMT platelets. A torch burn-through test revealed that the thermal gradient was 650 °C with the foam retaining its shape and therefore keeping the barrier intact.[208]

Table 8. Composite intumescent layer-by-layer fire protective coating on foams.

Substrate	Material	System	Number of units	Result	Reference
Foam	PU	PEI/GO/Melamine nanoparticles	2	Torch test: Self-extinguishment MLC: pHRR-39%; THR-12%; TSR-59%	[202]
		MMT/PAH/PSP	4 to 10TL	Torch test: Self-extinguishment MLC: pHRR-54% to -62%; THR-8%	[203]
		CH/APP	5	Torch test: no melt-dripping MLC: pHRR-24%; increased TSR	[204]
		CH/PAA-Kaolin		Torch test: self-extinguishment MLC: pHRR-53%; THR-34%; TSR-76%	
		CH/APP/CH/PAA-Kaolin		Torch test: self-extinguishment MLC: pHRR-67%; THR-40%; TSR-59%	
		CH/sodium hexametaphosphate/CH/MMT	5	HFT: Self-extinguishment MLC: pHRR-44%; THR-22%; TSR+11%	[205]
		CH/sodium hexametaphosphate/CH/SEP		HFT: Self-extinguishment MLC: pHRR-47%; THR-14%; TSR-43%	
		CH/sodium hexametaphosphate/CH/SiO ₂		HFT: no melt-dripping, enhanced charring MLC: pHRR-30%; THR-14%; TSR-27%	
		CH/APP	20	Torch test: no melt-dripping, enhanced charring MLC: pHRR-55%; THR-15%; TSR+113%	[206]
		CH/VMT	4	Torch test: Self-extinguishment MLC: pHRR-56%; THR-8%; TSR-57%	
		CH/VMT+CH/APP	4+20	Torch test: Self-extinguishment MLC: pHRR-66%; THR-11%; TSR+41%	
Aerogel	Cellulose nanofibrils	PAA/MMT+PDADMAC/Boehmite +APP/MMT	1	HFT: Self-extinguishment MLC : pHRR-50%; TSR-34%;	[207]
		CH/poly(vinylsulfonic acid)/CH/MMT	5	HFT: Self-extinguishment MLC: no ignition Burn-through torch test : back temperature maintained under 200°C	[208]

5.2.3.2 Passive barrier coatings

Passive barrier coatings are coatings that do not react to fire in the way intumescent coatings do, and whose protective effect stems from the compact layer formed by the residue. These coatings are composed of inorganic particles at a very high loading, and of a polymer or an organic part that plays the role of a sort of glue (or binder) between the particles. As a consequence, they are usually referred to as “brick and mortar” structures.

It appears that composite coatings have been less studied on textiles and flat substrates, probably because the protection offered by an inorganic-organic barrier is usually not high

enough. It is generally observed that the charring capacity is catalyzed and enhanced. The coating usually forms a coherent residue maintaining the shape of the substrate. Nevertheless, the polymer underneath is completely consumed. However, this barrier yields good results in the fire protection of foam substrates, therefore, a major part of the literature focuses on the protection of flexible polyurethane foams with layer-by-layer passive composite coatings.

Carbon-based particles, metal-based particles and silicon-based particles were used, but one or two papers reported more exotic chemistries.

The exciting thing about carbon-based nanoparticles such as graphene or carbon nanotube is that they are highly conductive, and as such, multifunctional materials are easily obtained with just one treatment, with electrical conductivity being the main property, and fire retardancy a welcome side-effect. But probably because of their high cost or difficult synthesis, carbon-based nanoparticles have been relatively less used than others, although they reach good fire retardant properties when used in passive layer-by-layer coating. For example, Davis et al used PEI-stabilized carbon nanofibers (CNF) and multi-wall carbon nanotubes (MWCNT) in a 4 BL layer-by-layer assembly with PAA on barrier fabrics and on polyurethane foam. It was found detrimental to HRR when applied to barrier fabric.[209] However, it led to a pHRR reduction of about 40 % on PUF and prevented pool fire in a MLC test.[210], [211] With MWCNT this result was further improved by using pyrene-modified PEI, with a reduction of pHRR of 68 %, as well as reduced and slowed down flame spread in both horizontal and vertical flame tests, using a 6 BL coating. It shows how the chemistry of the mortar can impact the protective behavior of the coating.[212] A similar result was obtained with 8 TL of chitosan-stabilized CNT, alginate, and MMT.[213]

Graphene oxide (GO) as a 2D material was also investigated to flame retard PUF. Its thermal stability as well as its potential high coverage attracted attention. Enhancing its solubility and its dispersion stability in water requires to use a dispersant such as PEI or sodium alginate before using it in a layer-by-layer process. All studies report pHRR reduction of at least 50 % with a few numbers of layers. For example, alginate-stabilized GO sheets layer alternating with PEI reduced the pHRR by 40 to 50 % with 2 to 5 BL. A synergistic effect was reported with SiO₂ particles (suppressing one of the two peaks of heat release rate observed for PUFs [214]), as well as with β -FeOOH nanorods.[215] Polydopamine-coated reduced GO (rGO)/PEI/PAA layer-by-layer achieved the same result with 3 TL.[216] 10 TL of CH/GO/Alg reduced pHRR by 60 %,[217] but the best result was obtained with 3 BL of PDADMAC/GO which completely prevented PUF combustion in cone calorimeter test and suppressed flame spread in a horizontal

flame test.[218] In this last study, the GO-coated PUF was submitted to a burn-through test and the thermal gradient obtained was the same as an incombustible silica aerogel. All works report a delay and a slowdown in the emission of combustible gases, as well as a reduction in total smoke production.

One limitation in using GO is that it is less thermally stable than rGO for example, which is mentioned in a comparative study by Pan et al.[219] To enhance its activity and thermal stability, Chen et al functionalized GO nanosheets with Phenoxycyclophosphazene and used them with PEI to coat a PVA sheet, showing HRR reduction at MCC test.[220]

Table 9. Passive composite layer-by-layer fire protective coatings with carbon-based nanoparticles.

Substrate	Material	System	Number of units	Result	Reference
Foam	PU	PAA/PEI-CNF	4	MLC: pHRR-40%; THR-21%	[210]
		PAA/PEI-MWCNT/PEI	4	MLC: pHRR-35%; THR-21%	[211]
		Pyrene-modified PEI/PAA-MWCNT	6	HFT, VFT: Self-extinguishment MLC: pHRR-68%; THR-3%; TSR-78%	[212]
		CH-CNT/MMT/Alginate	8	MLC: pHRR-69%; THR-3%	[213]
		PEI/alginate-GO/amino-modified SiO ₂	5	MLC: pHRR-51%	[214]
		PEI/alginate-GO/ β -FeOOH	5	MLC: pHRR-50%; THR+7%	[215]
		polydopamine-rGO/PAA/PEI	3	MLC: pHRR-49%; THR-5%; TSR-33%	[216]
		CH/GO/Alginate	10	MLC: pHRR-60%; THR-5%; TSR-31% Torch test : charring	[217]
		PDADMAC/GO	3	HFT: Self-extinguishment MLC: no ignition Burn-through torch test: temperature at the back maintained at 104°C	[218]
		PEI/alginate-GO	12	MLC: pHRR-72%; THR+18%; TSR-56%	[219]
		PEI/alginate-rGO		MLC: pHRR-65%; THR+7%; TSR-14%	
Polymer sheet	PVA	PEI/P,N functionalized GO	30	MCC: pHRR-60%; THR-67%	[220]
Textile	Barrier Fabric	PAA/PEI-CNF	4	MLC: Increased THR and pHRR	[209]
		PAA/PEI-MWCNT/PEI	4		

GO was also mentioned to be used in combination with β -FeOOH nanorods, which were also used in other systems for the fire protection of PUFs, either alone,[221] or in combination with MMT sheets.[222] In the first case, it was found to be more efficient in a trilayer coating with PEI and SA than in a bilayer coating with PEI only. It is believed to be due to an entangled network structure with whole coverage in the case of the trilayer coating, whereas only aggregate or island of nanorods were observed for the bilayer coating, failing to cover the foam. This morphology caused the foam to retain its shape and the pHRR was reduced by 62 % for 8

TL (15 % for 8 BL). The smoke production was delayed as well. MMT nanosheets were then added in the alginate solution to seek for a synergistic effect with the nanorods. Good coverage of the foams was obtained with either the FeOOH alone, MMT sheets alone, or both particles, with three cycles (cf Table 10). While MMT sheets alone already managed a 45 % reduction on pHRR, the combination with the nanorods further enhanced the reduction in HRR and managed to prevent shrinkage, with impressive smoke suppression properties not observed with MMT.

Other metal-based nanoparticles were found quite efficient when used in layer-by-layer protective coatings for PUF, and showed good to excellent efficiency in reducing HRR and suppressing smoke. Nanosheets such as MnO₂, α -ZrP and MXene (Ti₃C₂) were found to show particularly good fire retardant properties. Metal oxide particles were also used, such as TiO₂ nanotubes, aluminum oxide, and one particularly efficient α -Co(OH)₂ nanosheets containing system, that reduced the pHRR by 59 % with only one bilayer with sodium alginate. TiO₂ nanotubes were used in an 8 TL coating with chitosan and alginate and reduced the flammability of the PUF substrate at cone calorimeter test, by reducing the pHRR by 70 %, and the TSR by 41 %. However, the THR was barely reduced, revealing that the emission of fuel was slowed down rather than impeded.[223] Similar performances in HRR were obtained with 6 BL of PEI and PAA-stabilized Aluminum TriHydroxide (ATH) particles (pHRR reduced by 64 % and no THR reduction, 85 % residue), but without any smoke reduction.[224] A delayed and slowed down emission of fuel was also observed for nanosheets particle, starting with MnO₂ used with PEI/Alginate, where a 6 TL coating reduced the pHRR by 47 % but not the THR. Smoke and harmful gases emission were reduced.[225] The same performances were achieved with a 6 TL CH/Alg/ZrP coating with high CH and Alg solution concentration, the pHRR being further reduced to 71 % by an additional 3 TL.[226] However, another study with MoS₂ nanosheets points out the role played by the chemistry of the particle. 8 BL of CH/MoS₂ also reduced the pHRR by 71 %, as well as smoke and harmful gases emission, yet, this time, a reduction of THR by 20 % was observed.[227] Further reduction in THR was observed when switching MoS₂ with MXene (Ti₃C₂) nanosheets. A 66% reduction in THR and a 71% reduction in TSR were observed, despite a worse performance in term of pHRR (-57 %).[228] 1 BL of Alginate/ α -Co(OH)₂ was enough to reduce the pHRR by 59 % (65 % for 2 BL). It is attributed to the formation of a protective char thanks to the catalytic action of Co(OH)₂. However, increasing the number of bilayer and therefore the nanosheets' concentration led to a detrimental effect that further catalyzed the decomposition of the char, which was thus less protective.[229]

Table 10. Passive composite layer-by-layer fire protective coatings with metal-based nanoparticles.

Substrate	Material	System	Number of units	Result	Reference
Foam	PU	PEI/ β -FeOOH/alginate	8	MLC: pHRR-62%; THR=; TSR-21%	[221]
		PEI/alginate-MMT/ β -FeOOH	3	MLC: pHRR-47%; THR-10%	[222]
		PEI/alginate-MMT		MLC: pHRR-45%; THR=	
		PEI/ β -FeOOH		MLC: pHRR-14%; THR=	
		CH/TiO ₂ /Alginate	8	MLC: pHRR-70%; THR-13%; TSR-41%	[223]
		PEI/PAA-ATH	6	MLC: pHRR-70%; THR=; TSR+64% Torch test: self-extinguishment	[224]
		PEI/MnO ₂ /alginate	6	MLC: pHRR-47%; THR=	[225]
		CH/ α -ZrP/alginate	9	MLC: pHRR-71%; THR=	[226]
		CH/MoS ₂	8	MLC: pHRR-70%; THR-17%; TSR-33%	[227]
		CH/MXene(Ti ₃ C ₂)	8	MLC: pHRR-57%; THR-66%; TSR-71%	[228]
		Alginate/Co(OH) ₂	1	MLC: pHRR-59%; THR=	[229]

Other nanosheets were used in layer-by-layer coating to fire retard polyurethane foams. Graphene-like alginate-stabilized h-BN nanosheets, used in a 20 BL layer-by-layer coating with BPEI applied on PUF, showed a reduction of pHRR and of the peak of CO production by about 50 %, with increased charring effect, despite an increased smoke production.[230] Apart from this study, h-BN was proven to be a very promising material for fire protection, as it allows to lower the pHRR of PUF by 54 % with only a single bilayer (PEI/h-BN). Interestingly, it was found to also have UV protection ability, and it also barely impacted the mechanical properties of the foam substrate.[231]

More exotically, Lanthanum PhenylPhosphate nanosheets were reported to reduce the pHRR by 71 % with 6 BL with BPEI acting as mortar. It was also accompanied by a slight THR decrease (15 %), because of slightly increased residue. This decrease in pHRR is suggested to be because of the delay in emission of volatile fuel as shown by the mass loss curve.[232] Layered Double Hydroxide (LDH) as clay-like nanosheets were also synthesized and used. MgAl-LDH and NiAl-LDH-including 12 TL with CH and Alg reduced the pHRR by 65 and 75 % respectively with a THR reduction of 25 % due to enhanced charring (around 20 % residue), with an enhanced catalytic carbonization effect brought by the presence of the Ni atom.[233] MgAl-LDH only decreased the pHRR by around 40% in a 5 BL nanocoating, but completely suppressed the second HRR peak of PUF burning. With a residue of 20 %, the THR was also slightly decreased.[234] However, this effect was enhanced with a 2 TL coating. As the top of the sample burnt completely, the barrier created was protective enough to prevent the back of

the sample from burning, reaching a residue of 71 %.[235] All coatings were able to keep the open-cell structure of the exposed PUF, as well as the fiber structure of cotton fabric in one occurrence by Pan et al. They showed that an 20 BL PEI/LDH coating could enhance the charring capacity of a cotton sample in a vertical fire test, and the pHRR and THR were reduced in a MCC test.[236]

Table 11. Passive composite layer-by-layer fire protective coatings with nanosheets.

Substrate	Material	System	Number of units	Result	Reference
Foam	PU	PEI/alginate-h-BN	10	MLC: pHRR-50%; THR=; TSR+107%	[230]
		PEI/h-BN	1	Torch test: self-extinguishment MLC: pHRR -54%THR =	[231]
		Alginate-Lanthanum phenylphosphate/PEI	6	MLC: pHRR-70%; THR-15%; TSR-15%	[232]
		CH/alginate-MgAl LDH	12	MLC: pHRR-66%; THR-24%; TSR-74%	[233]
		CH/alginate-NiAl LDH		MLC: pHRR-75%; THR-27%; TSR-84%	
		PAA/BPEI-MgAl LDH	5	MLC: pHRR-40%; THR-14%	[234]
		PAA/MgAl LDH/PEI	2	MLC: pHRR-40%; THR-30%	[235]
Textile	Cotton	Alginate/MgAl LDH	20	VFT: cohesive residue MCC: pHRR-35%; THR-26%	[236]

Silicon-based nanoparticles were particularly studied. Some synergistic systems with clay or silica were already mentioned, and while some systems were proven more efficient, their ease of use, their availability and environmental-friendly nature make them a good and often favored compromise. First, the combination of anionic POSS with either cationic POSS or aminopropyl silsesquioxane oligomer reduced the intensity of flaming and increased the residue.[237] Silica used with BPEI and UV-cured PU allows PC sheets to self-extinguish in horizontal flame test.[238] Then, Si and P composite coatings were applied on Poly(acrylonitrile) (PAN) fabrics. If 6 BL n-propylammonium chloride POSS/APP only reduced the pHRR by around 20 %, [239] 10 BL of Silica gel/phytic acid managed to reduce pHRR by 66 % and THR by 73 % thanks to an enhanced charring.[240] In the first study, the increase in CO production hinted at a barrier mechanism preventing oxygen heat and fuel transfer at the interface, while the second study combined the barrier effect from silica with charring enhancement from phytic acid. N-propylammonium chloride POSS was also used with sodium montmorillonite (MMT) clay platelets in the fire protection of PET fabric with a 5 BL coating. In addition, with melt-dripping suppression and reduced burning rate, the combustion was slowed down, which was evidenced by the reduced HRR (reduction of 50 % of the pHRR).[241] A few other systems using MMT have already been mentioned, and it is indeed clearly the most studied clay in layer-by-layer

coating for fire protection. A 20 BL starch/MMT coating did not prevent cotton fabric to be consumed, but the char layer was protective enough to preserve the fabric structure, slow down the burning rate in a vertical flame test, and attenuate the HRR in a low heat flux cone calorimeter test.[242] On Polyester, 4 QL of CH/MMT/CH/TiO₂ reduced the pHRR and THR by 48 % and 36 % respectively.[243] Batool et al. investigated epoxy-based composite MMT layer-by-layer coating combined with TriPhenylPhosphate, which induced a 25 % reduction in pHRR.[244] The burning length of a PI fabric was reduced with a 20 BL Poly(N-benzyloxycarbonyl-3,4-dihydroxyphenylalanine)/MMT, even after washing,[245] but a 8 TL PEI/MMT/PAA coating on a barrier fabric was found to be detrimental to the HRR.[209]

The same system on PUF only decreased the HRR by 17 %, and while it might seem like an insignificant result, it was one of the first studies of a LbL MMT-based coating on PUF, and it had the advantage of highlighting the interest of the system by showing that with much less FR material, and with an environmental friendly method, results similar to those observed for commercial-used PUF fire retardant fillers were obtained.[209], [246]. And indeed, it was possible to improve this behavior by adjusting the concentration of MMT in the solution, and to completely suppress the second HRR peak linked to polyol decomposition. While the pHRR was only reduced by 30 %, the average HRR was reduced by 75 %.[247] Even more impressive, an optimized coating (pHRR reduction of 42 % in cone calorimetry) could reduce the pHRR by 53 % in real scale mock-up test with only 5 BL.[248] A 10 BL thick CH/MMT led to similar results. The pHRR was reduced by 52 %, and attenuated the HRR in general. The thick protective char layer is believed to be the cause for this delayed decomposition, which however only provoked longer burning with no THR loss, as everything was consumed.[249]

The use of other clays than MMT, not platelet-like but with other structures, should also be mentioned. Halloysite is a type of clay which rolls down on itself, creating Halloysite nanotubes (HAL) with negative charge on the outside and positive charge on the inside.[250] Also, sepiolite is a natural clay found under the form of needle. Both were used in layer-by-layer coatings and showed good efficiency in protecting PUF against fire. While the HAL-based coating reduced pHRR by 62 % and TSR by 60 %, it did not reduce THR as all PU was consumed.[251] But, the barrier formed by the sepiolite-based coating seems more effective as the pHRR was decreased by a further 14 % and the THR was reduced, as it prevents the complete combustion of the sample. This study also provided some clues as to the smoke suppressing ability of clays, which seem to be releasing water when exposed to a temperature stress.[252] Other clay platelets were used to protect flammable substrates: Kaolin and Laponite

were already mentioned, but among them, vermiculite (VMT) platelets might be more efficient, as evidenced in this study by Cain et al. With only 1 bilayer of PEI/VMT, pHRR was reduced by 54 %, the foam structure was kept, and the THR was slightly decreased as the second HRR peak is suppressed. In the meantime, it took 4 BL of PEI/MMT layer-by-layer coating to reach the same results.[253] There, it is suggested that VMT might act as a char catalyst. VMT was also used recently in an 8 BL LbL treatment in combination with chitosan. The fire performances were evaluated against a variety of fire scenario. While MLC showed a reduction of pHRR and TSR by 53 % and 63 % respectively, the foam also self-extinguished after 10 s exposure to a hand torch. It also demonstrated thermal shielding behavior in a burn-through fire test. It was exposed to a 116 kW/m² heat flux using a butane torch, and sustained the harsh conditions for 900 s. Thermocouples embedded in the foam recorded a thermal gradient of more than 200°C across the 2.5 cm thick material.[254]

Other studies were conducted, one on Polystyrene plates, whose ignition from a butane torch was prevented by a thick 8 BL CH/MMT or an 8 BL CH/VMT nanocoating.[255] On PUF, 2 BL of a VMT/Cellulose Nanofibrils was enough to prevent melt-dripping. The carbonaceous outer layer formed protected the sample from burning, and the highly stable char formed by the Cellulose Nanofibrils led to a better barrier than a 2 BL CH/VMT coating.[256] It could also be linked to a thermal shielding effect, as proposed by the work of Carosio et al, where a self-standing film of Cellulose Nanofibrils/MMT could maintain the temperature at the back of the so-called paper under 260°C for 5 min while the front was subjected to a small butane torch. In this study they relate this to the charring of Cellulose Nanofibrils as well as to the delamination of the platelets.[257]

Table 12. Passive composite layer-by-layer fire protective coatings with Silicon-based nanoparticles.

Substrate	Material	System	Number of units	Result	Reference
Foam	PU	Poly(o-cresylglycidylether)-co-formaldehyde/NH ₂ -MMT/PEI-triphenylphosphate	12	MLC: pHRR-25%; increased TTI	[244]
		PEI/MMT/PAA	8	MLC: pHRR-17%; THR=	[244]
		PEI/MMT/PAA	3	MLC: pHRR-30%	[247]
		PAA-MMT/PEI	5	MLC: pHRR-42% Mock-up real scale test: pHRR-53%	[248]
		CH/MMT	10	Torch test: no melt-dripping MLC: pHRR-52%; THR-10%	[249]
		BPEI-HAL/PAA-HAL	5	Torch test: no melt-dripping MLC: pHRR-62%; THR=; TSR-60%	[251]
		PEI/alginate-Sepiolite	6	MLC: pHRR-76%; THR-27%; TSR-27%	[252]
		PEI/VMT	1	MLC: pHRR-54%; THR-13%; TSR-31% (needs 4BL CH/MMT to reach these results)	[253]
		Cellulose Nanofibrils/VMT	2	Torch test: no melt-dripping	[256]
		CH/VMT	8	Torch test: self-extinguishment MLC: pHRR-53%, THR-17%, TSR-63% Burn-through test: 245°C thermal gradient across the foam, sustained the 116 kW/m ² heat flux for 900 s	[254]
Textile	Cotton	Starch/MMT	20	VFT: cohesive residue MLC: pHRR-21%; THR-15%; reduced TTI	[242]
		Cationic POSS/anionic POSS	20	VFT: cohesive residue MCC: pHRR-11%; THR-17% Pill test: smoldering, 7x53mm char	[237]
		Aminopropyl silsesquioxane/anionic POSS		VFT: cohesive residue MCC: pHRR-20%; THR-23% Pill test: smoldering, 7x20mm char	
	Acrylic	Cationic POSS/APP	6	VFT: no melt-dripping, limited burning LOI: 22% MLC: pHRR-23%; THR=	[239]
	PET	Cationic POSS/MMT	5	HFT: no melt-dripping, reduced burning rate MLC: pHRR-50%; THR=; TSR=; reduced TTI	[241]
		CH/MMT/CH/TiO ₂	5	MLC: pHRR-48%; THR-36%; reduced TTI	[243]
	Barrier fabric	PEI/MMT/PAA	8	MLC: Increased pHRR and THR	[209]
	PI	Poly(benzyloxycarbonyl-3,4-dihydroxyphenylalanine)/MMT	20	VFT: reduced burning length	[245]
	PAN	Silica gel(APTES)/PA	10	MLC: pHRR-66%; THR-73% LOI: 33%	[240]
Bulk polymer	PC sheet	PEI/anionic SiO ₂ /cationic SiO ₂ /UV-curable aliphatic PU	5	HFT: Self-extinguishment, no melt-dripping	[238]
	PA6 sheet	PAH/MMT	20, 40	MLC: pHRR-60%; THR=; TSR-57%; increased TTI	[258], [259]
	PS plate	CH/VMT+amine salt treatment for increased thickness	2	Burn-through torch test: Self-extinguishment (8BL: no ignition)	[255]

5.2.3.3 *Thoughts on the mechanism*

The mechanism of passive barrier coatings is not very clear, although some thoughts have been given to it in the literature. However, most point out a condensed phase mechanism. It appears that the composite nanocoatings are able to form a shell that maintains the substrate's shape. This shell, like an exoskeleton, acts as a physical barrier to delay and slow down the release of fuel into the flame, therefore effectively reducing the HRR during a cone calorimeter test (this has been verified through mass loss curves). In some cases, an increase of the time to ignition is observed. Apaydin et al. attributed this to the formation of a “high performance, stable, and flexible carbonaceous-silicate char barrier at the surface of the sample” which delay mass transfer of degradation products.[132] In some extreme occurrences, the protection formed prevents the ignition completely. In other cases, no effect on the time-to-ignition was observed, or the presence of the coating caused it to decrease. This might be due to several reasons. First, the barrier might not be thick or stable enough to delay the transfer of flammable products. Then, it can form cracks,[191] or be discontinuous, or the presence of particles can catalyze the degradation of the substrate.

This shell also prevents melt-dripping (in an open flame scenario) or pool burning (in a radiative scenario), therefore forcing the combustion (if any) of the polymer inside the exoskeleton. As a consequence, the stronger the barrier the better, and it should form early enough to be able to act efficiently (before substrate decomposition). This mechanism was investigated in the work by Apaydin et al., where they show how a PAH/MMT nanocoating could act to protect a PA6 sheet, by decreasing the pHRR by 60 %.[258] They evidenced the early degradation of PAH, and that the MMT-reinforced char layer could act as a trap to combustion gases, which helped expanding the protective layer.[259]

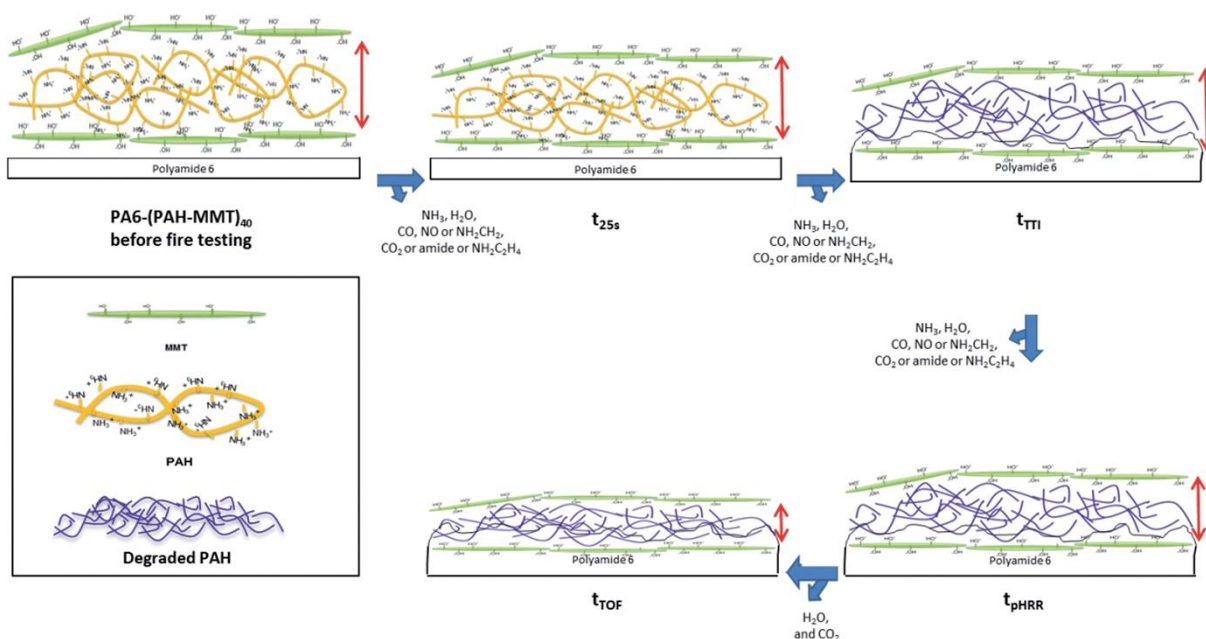


Figure 6. The mechanism of (PAH-MMT) $_n$ flame retardant coating. Reproduced from Ref.[259] with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.

Indeed, the most efficient systems seem to be those producing a thermally stable, strong, and continuous char. It was suggested from Raman analyses that the more protective coatings gave residues with a high graphitization degree, which is attributed to a higher thermal stability of the char. The higher protective ability is ascribed to a better barrier effect because of a more compact residue. This has to do with the chemistry of the mortar and its inherent charring ability, or to the presence of catalytic sites favoring the formation of a graphitic char.[138], [152], [181], [216], [223], [229], [230], [232] This result may be surprising, because it was proven that an ordered char was more prone to cracks which was detrimental to fire properties.[260], [261] It is probable that the presence of particles maintains the char structure and improves the mechanical properties, but this point is not addressed in the mentioned papers.

The presence of phosphorus seems to help strengthen the char formed. This can be either by catalyzing its formation (therefore protecting the substrate before its decomposition), by promoting the decomposition pathways leading to the formation of aromatic carbon structures, by crosslinking, by formation of phosphorus-containing coating, or formation of inorganic glasses.[262] In the literature, it is also suggested that the presence of phosphorous can prevent the oxidation of the char at high temperature.[263], [264] It was also reported that chars containing phosphorous improve the capacity of the carbon layer to prevent volatile species and

melting polymers from diffusing through it.[265] In addition, continuous coverage and higher thickness obviously allow to reach better performances. Consequently, better results are reached by adjusting the composition, pH and concentration of the deposition solutions to influence the physico-chemical phenomena driving the coating process (amine salt to increase thickness; polymers with higher molecular weight; higher concentrations of the solutions of nanoparticles etc.). Packing density of the particle is also important. The chemistry of the nanoparticle also seems to impact the effect of the nanocoating on the fire protection of the substrate. It seems that particles with believed catalytic ability such as metal nanoparticles or metal-rich clays are more efficient. It means that they can catalyze the formation of a compact and thermally stable char more easily. Less layers are thus required for good protection.

Usually inside the shell produced by the coating, the flammable substrate underneath is completely consumed, and therefore, the THR is not reduced. This is the reason why most composite coatings only slow down flame spread rather than stopping it, at least with textile or paper substrates. With foam substrates, however, the porous char layer formed on top is sometimes protective enough to prevent the combustion of the flammable material underneath, and less fuel means less heat produced. Smoke suppressing ability of some particles was pointed out, and it was suggested to be linked to either water release (in one occurrence with sepiolite clay), mesoporous nature of the particle, or catalytic activity of the particle, which in case of metal-based particles also led to less harmful gases being released. Finally, some works suggest that the protective effect of the films comes from a thermal barrier effect, although it was not proven in-situ.

Recent work on PUF revealed the mechanism of action of passive composite coatings. An 8 BL CH/VMT LbL treatment was found to have a thermal shielding behavior. This was attributed to the creation of an exoskeleton on the side directly impacted by the flame or the thermal constraint. This empty porous structure shields the rest of the material from the worst of the stress, and serves to bring the temperature down deeper in the foam. This was measured in a high heat flux burn through fire test by thermocouples embedded in the material. TGA of the residues from a show the increasing char content across the sample, which shows that the thermal protection was sufficient to promote char formation.

The increased char content adds another thermal protection. As a result, a thermal gradient of 245°C was recorded (measured by embedded thermocouples). The back side of the coated PUF was therefore protected by the front side of the sample, to the point where plain PU was preserved at the end.[254]

To conclude, layer-by-layer coatings are very promising for the fire protection of flammable substrates. One reproach can be made to this type of process, as it requires considerable amount of water, that need to be changed regularly. However, the main technological lock in the industrial application of layer-by-layer coating for fire safety is the high number of processing steps. While research has been developed to accelerate the process to industrially accepting times, or to design machines towards its automation (see 5.1), one of the most promising approach consists in reducing the number of processing steps drastically. This approach has already been explored in a few papers (see for example references [229], [231], [253].)

6. Exploring new opportunities: alternatives to layer-by-layer thin coatings with similar mechanisms

6.1 One-pot nanocomposite coatings

6.1.1 Polyelectrolyte complexes

To eliminate the inconvenience of depositing thin layer-by-layer coatings step-by-step, one-pot strategies have been explored. Polyelectrolyte complexes of intumescent systems have been deposited on different fabrics. Two polymers of opposite charge are mixed together in distilled water to form an insoluble complex which is adsorbed afterwards on the substrates by simple immersion for a definite soaking time. Polyethyleneimine and Poly(sodium Phosphate) were combined together on cotton fabric with different soaking times. Their action reduced the pHRR from 17 % to 57 %, as well as the THR (up to 77 %) in MCC experiments (the reduction was improved by increasing weight gain). Self-extinguishment was obtained in vertical flame tests starting from 23 % weight gain, while coherent charring was observed for lower complex quantities.[266] The soaking time required to reach this mass was reduced (from 10 min to 30 s) by increasing the complex concentration in the treating solution, and the performance and durability of the coating was improved with acid pH curing. This way, the reduction of pHRR with curing at pH 2 reached 81 % while the THR was reduced by 88 %. Again, it is accompanied by self-extinguishment in vertical flame testing.[267] Similar performances were obtained for a complex with poly(allylamine) instead of PEI (pHRR -78 %, self-extinguishment), but they were more limited for synthetic fabrics (pHRR reduced by around 30 % for Polyester-cotton blends and polyester).[135] Thanks to the high P quantities, a Poly Electrolyte Complex (PEC) of phytic acid and PEI on wool reduced pHRR by 39 %, THR by 79 % and smoke density of wool fabric samples, while increasing the LOI to 36.8 %.[268] Bio-based resources were also

used and chitosan and phosphorylated chitosan were deposited in a one pot process on PA66 fabrics, along with sodium polyacrylate for UV-crosslinking with an attempt of increasing durability. A 10 min impregnation increased LOI up to 22 % and the suppression of dripping allowed reaching the V-1 level rating at UL94 test. In that case, however, the layer-by-layer coating was still more efficient than the one-pot process in a cone calorimetry test, as it did not reduce the flammability parameters.[149] While it did not rely on polyelectrolyte complex, another study took advantage of the precipitation of poly[1,4-diaminophenylene-tris(dimethylhydroxymethyl)phosphine] when para-phenylenediamine and tetrakis(hydroxymethyl)phosphonium chloride are mixed together. An aqueous solution of this specie was deposited on one side of a cotton sample by spray coating. Despite the fact that all faces were not covered, charring was observed in vertical flame testing, and self-extinguishment when exposed to a horizontal flame. MCC experiments revealed a reduction of 45 % and 63 % of pHRR and THR respectively.[269]

6.1.2 One-pot composite thin coatings

Composite dispersions were also deposited by dip-coating on several substrates to produce thin protections taking advantage of the physical protection offered by composite structures. For example, halloysite nanotubes were dispersed with aniline in water on cotton and acrylic fabrics, and aniline was further polymerized. This coating reduced the burning rate in vertical flame testing.[270] The same principle was applied by mixing PDMS precursor with MWCNT/ZnO complexes on paper filter and showed enhanced charring.[271] A mixture of a commercial polymeric binder, graphite, TiO₂ nanoparticles (for hydrophobicity) APP and N-[3-(trimethoxysilyl)propyl]-ethylene diamine stopped the flame spread thanks to the char layer and increased the LOI up to 24 % when deposited on furniture fabric.[272] The same principle of mixing all the required ingredients to obtain a thin fire retardant film in a single pot and just impregnate the substrate by dip-coating was also applied on PU foams by Davis et al, who mixed sodium polyborate, starch and MMT by squeezing the substrates in an aqueous mixture of the three ingredients. This resulted in quite high weight gains, but also in reductions of 66 % to 75 % of the pHRR (no reduction in THR) in cone calorimetry tests depending on the formulation. What is interesting is that a real scale mock-up test of an armchair filled with treated PUF showed even better results, with similar reduction in pHRR depending on the furniture fabric, but also up to 71 % reduction in THR, due to the protecting effect of starch and sodium polyborate slowing down the pyrolysis.[273]

However, the most interesting studies deal with the deposition of high filler content nanocomposite thin coatings. Some works propose making the composite before gluing it to the substrate by mean of an adhesive or by thermopressing.[274], [275] In a study by Carosio et al., a 70 μm film of cellulose nanofibrils and MMT prepared by vacuum filtration and hot-pressed on epoxy glass fibers composites sustained the flame of a butane/propane torch, while keeping the temperature at the back of the substrate below 100 $^{\circ}\text{C}$ (whereas without coating the temperature was kept at 200 $^{\circ}\text{C}$ with no flame penetration).[257]

Another study reached good results by immersing a PU foam in GO suspension before self-polymerizing dopamine in-situ. Kim et al. obtained a thin PDA/GO coating which brought self-extinguishment behavior and protected the samples inner core in a vertical flame test, and reduced the pHRR in cone calorimetry by 65 %.[276] Researchers have taken inspiration from nacre, which has a hierarchical organized structure composed of 95 % of aligned aragonite (CaCO_3) platelets linked together by proteins. The first goal of developing composites mimicking nacre was to make materials with interesting mechanical properties.[277] However, their high mineral content obviously raises an interest in using them for fire protection. While layer-by-layer is one of the methods to make nacre-like nanocomposites, one-pot strategies were developed to deposit thin coatings with high filler content mimicking nacre, that rely on mixing platelet-like nanoparticles with a polymer binder in concentrated slurries. Platelet-like nanoparticles tend to organize themselves by dip-coating, doctor-blading, painting, solution casting, vacuum-filtration processes..., allowing to obtain high scale organized nanocomposite with more than 50 % of filler content. All techniques are not appropriate for coating substrates, but some such as dip-coating, doctor-blading and painting can be used easily, especially on textiles and polymer films or plates, although some one-pot self-assembly on foams have been reported.[278] GO and functionalized cellulose were mixed together and deposited on PU foam, wood bars and PP bars, with different GO content. Structured coatings were obtained, and while a single step was enough for PU foam to reach a significantly reduced flammability, several dip-coating steps were required to coat wood and PP bars efficiently. While it defeats the purpose of having a one pot coating, LOI values were increased, and a V-0 rating was obtained in a modified UL94 test with an alcohol lamp.[279] Xie et al. also mixed carboximethyl chitosan with MMT modified with epoxysilane, and deposited the mixture on PET films, cotton fabric and PUF, with several dipping repetitions on PET films. Self-extinguishment was observed in vertical flame testing with an alcohol lamp for PET and cotton fabrics. The flammability of PU foam under cone calorimetry was reduced as pHRR and THR decreased by

more than 80 %, and extensive residue was produced because of immediate extinction.[280] MMT as a natural platelet-like nanoparticle was extensively studied in high-filler nanocomposite one-pot coatings. Carosio et al coated CH/MMT complex on acrylic fabrics by several doctor-blading steps to coat both sides of the sample and reach the desired weight gain. The coating reduced pHRR, THR and TSR by 62 %, 49 % and 49 % respectively in a cone calorimetry test, and increased the time to ignition. It also slowed down flame spread in horizontal flame test and suppressed dripping.[281] Walther et al. were pioneers in developing large scale one-pot nacre-mimicking structures, and they used either paper-making process, doctor-blading or simple painting. The shear-force of the last two systems was enough to align MMT platelets covered in PVA.[277] The same concept was developed to produce carboxymethylcellulose/MMT films from mixtures at 60/40 w/w proportions,[282] which were then applied on cotton fabrics by slowly dragging the fabrics through a 5 wt% concentrated slurry. pHRR and THR were reduced by 37 % and 44 % respectively in cone calorimetry, and self-extinguishment and reduced burning rates were observed at vertical flame test. The cotton samples also resisted to a hand-held torch test and shrinkage was prevented.[283]

Flow-induced self-assembled coatings containing 70 wt% of MMT nanosheets with PVA were deposited on PU foams by dipping them in the mixture of both components with glutaraldehyde as cross-linking agent, and letting them to hang dry. The samples resisted a 10 s hand-torch test.[284]

The use of cross-linked structures is usually carried out as a mean to increase the durability of the treatment on textile,[149] even if some studies on alginate and PEI/o-alginate cross-linked with phosphoric acid, or alginate coatings cross-linked with metal ions were more focused on the idea of taking advantage of the crosslinker as a potential active additive.[172], [285], [286] Crosslinking is known to enhance the thermal stability, and it could help enhancing the char forming ability of nanocomposite coatings. In this regard, the use of highly cross-linked structures such as hydrogels could be one way, once dried, to achieve such structures in order to improve the performance of nanocomposite thin coatings, while still keeping a one pot procedure.

In the next part, definition and use of hydrogel and dried hydrogel against fire are described.

6.2 *Hydrogels and polymer networks for fire protection*

6.2.1 Definition and application

A hydrogel is a three-dimensional cross-linked hydrophilic polymer network swollen in water. It is kept together and rendered insoluble by crosslinks (or tie-points, or junctions) which can be covalent bonds, ionic forces, hydrogen bonds, entanglements, crystallites, etc. They have the ability to absorb and retain a large quantity of water. In fact, the primary component of hydrogels is water, while the polymeric network constitutes a small part of the material. According to their method of crosslinking, they can be classified as chemically cross-linked (formation of the hydrogel via the establishment of covalent bonds between the polymer chains) or physically cross-linked (the network is maintained via physical forces such as ionic interactions, for example).[287] The latter is of particular interest because of the usually soft conditions in which they are formed. A broad variety of polymers can be used to form hydrogels, both synthetic and natural. Poly(2-hydroxyethyl methacrylate) (pHEMA) is one of the most well-known polymer and forms hydrogels via radical cross-linking. PVA and polysaccharides such as chitosan, carrageenan, agarose, collagen, gelatin or alginate are also used to form hydrogel materials through chemical or physical cross-linking. Most applications of hydrogels lie in the biomedical fields, and they are used for contact lenses, drug delivery systems, tissue engineering, wound-healing bio-adhesives, artificial skin etc.[288] They are also used in food and agricultural applications, as well as in soft robotic (conductive sensors for electronic devices, flexible displays...).[289] Last but not least, they also have applications in fire science.

6.2.2 The use of hydrogels against fire

First, hydrogels are largely used as fire extinguishments and prevention systems. They can be dispersed thanks to a traditional sprinkler system, for example. It is required that they have a high and rapid water uptake and high retention capacity. They are mostly thought of as fire resistant materials. In mines for example, they are used to extinguish coal combustion and prevent the spread of the fire by preventing coal oxidation. Overall, they are supposed to limit the temperature of the ignition source, reduce thermal radiation and reduce the amount of CO gas generated. Fire extinguishing gels are also designed to be able to cover the burning materials completely. Most gels are copolymers synthesized from at least an acrylamide or acrylamide-derived monomers,[290], [291] with eventual mineral fillers [292]–[294] and fire

retardants.[295] Large scale use of hydrogel has been studied for wildland fires extinction with cellulose-derived/silica and fire retardant formulations,[296] while thermosensitive hydrogels (gel forming above a determined temperature) synthesized from N-isopropylacrylamide and hydrophilic monomers seem promising for this application.[297], [298]

As fire resistant materials, they are also used as active protection solutions for firefighting. For example, protective clothing or protective covers have been imagined using tough hydrogels as textile laminates. The idea behind this is that the hydrogel should keep the temperature low enough and absorb enough heat to be able to maneuver during a fire for a determined amount of time (until it is completely dehydrated). It requires a large amount of hydrogel to be able to keep the protection long enough.[299], [300] Protection of flammable materials for a short while during fire can also be obtained with hydrogels. For example, an electronic circuit with conductive hydrogels could work during a fire for a short moment.[301] Hydrogels casing for flammable oil transport can also be envisioned.[302] Very recently, a fire resistant robot skin made from a gelatin hydrogel filled with carbon nanotubes was developed. It aims at manipulating and extracting objects from a fire scene.[303] Also very recently, a durable hydrogel fire resistant coating has been proposed for fireproof clothing, trees or structures. A 2 mm thick plate could prevent flame penetration for 40 s. Interestingly, the hydrogel was kept from drying thanks to high concentrations of a highly hydratable salt (LiCl).[304]

Hydrogels are therefore very promising for fire protection. Yet, despite the exciting perspective of having high quantities of water sealed away for fire retardant purposes, they are mostly used as active fire protective systems, although one study reports of a starch-g-poly(butyl acrylate)/mica hydrogel as a 3 mm thick fire protective coating on wood (the coating significantly increased the time to ignition without decreasing the pHRR too much in a MLC test).[305] Two other studies by Geoffroy et al. also demonstrate their high potential as fire retardant materials. Agar-agar, PVA (with borax cross-linking) and alginate hydrogels were incorporated in 3D-printed EVA-based sandwich multi-materials and showed very good performance at MLC test (long time to ignition with the hydrogel alone, and fast self-extinguishment with fire retardant such as vermiculite or potassium carbonate).[306] However, studies remain scarce. The reason is that to be used as fire retardant materials, and *a fortiori* as fire retardant coatings, a drying step is necessary for practical purposes. Depending on the drying method, two types of materials can be obtained, namely aerogel or xerogel.

6.2.3 Aerogels

Aerogels are obtained by replacing water by air. Two methods can be employed. Freeze-drying consists in freezing water (usually at between $-70\text{ }^{\circ}\text{C}$ and $-80\text{ }^{\circ}\text{C}$, but it depends on the sample), followed by the sublimation of the ice crystals by rising the temperature below $0\text{ }^{\circ}\text{C}$. It creates porous structures whose morphologies depend on the formation of the water crystals during freezing. It can be used as a method of crosslinking for certain systems such as polyvinyl alcohol. However, the most thrilling approach is to obtain aerogels via supercritical drying. During this procedure, water is first replaced by alcohol, and then by supercritical CO_2 . While expensive, it is an environmentally friendly method which creates materials with unexpected properties, such as astonishingly low thermal conductivity. While the most known aerogels are made from silica network synthesized with a sol-gel procedure and dried with supercritical CO_2 , they have poor mechanical properties. Even if there are some reports of good fire retardant graphene aerogel,[307] a large portion of the research on aerogel materials focuses on organic polymers, which are made through freeze-drying hydrogels or viscous aqueous solutions. Crosslinking often occurs during freeze-drying. As such, obtaining polymer aerogel with low flammability still requires the same strategies as their filled counterparts, but they easily reach LOI values higher than 30, and very low pHRR at MLC tests, even presenting non flaming combustion in some occurrences. First, they can be made from high performance polymers such as PI [308], [309] or PolyBenzoxazole (PBO).[310] Then, they can be formulated with fire retardant fillers. The advantage of hydrogels is that they allow reaching high filler content, for example with clays. Polysaccharides aerogels are often studied. For example, cellulose aerogels can char when they are subjected to the flame of a lighter,[311] and have quite low pHRR (around 120 kW/m^2 [312]) in MLC test, but still need the addition of magnesium hydroxide, [313] citric acid crosslinking [314] or LDH [312] to reduce their flammability. Wood fibers with palygorskite make aerogels with pHRR under 30 kW/m^2 . [315] Cellulose NanoFibers (CelNF) are also largely used and combined with sodium carbonate,[316] graphene oxide mixed with ZrP [317] or sepiolite,[318] or in a mixture of carboxymethylcellulose, APP and MMT.[319] Sometimes an additional crosslinking step is performed, for example by heat treatment with the addition of N-methylol dimethylphosphonopropionamide (MDPA) and 1,2,3,4-butanetetracarboxylic acid (BTCA).[320] Also reported are the addition of Polyaniline and phosphoric acid,[321] PEI and 3-Glycidoxypropyltrimethoxysilane in a formulation of CelNF and hydroxyapatite,[322] or MMT and melamine formaldehyde resin with boric acid crosslinking (which reach a LOI superior to 85 %).[323] The additional crosslinking usually

decreases the flammability of the material further, which translates in a reduction of PHRR when compared to the system without cross-linkers.[324] Melamine formaldehyde is used quite frequently to improve the flammability of polymer aerogels, for example with pectin,[325] alginate,[326] or PVA.[327] PVA is quite well-known for forming cross-linked structures upon freeze-drying, and as such was extensively used in aerogel formulation. However, its flammability still requires additional flame retardants such as CelNF and APP,[328] laponite and fly ash,[329] Laponite, Halloysite nanotube, SiO₂,[330] APP and ZrP,[331] APP and MXene,[332] or APP and boron nitride nanosheets.[333] MMT is used quite a lot in PVA fire retardant aerogel, either alone [330] or in combination with CelNF,[334] gelatin,[335] or with APP, silica gel and K₂CO₃. [336] Again, an additional cross-linking step with chemical cross-linkers (borate,[337], borax, or glutaraldehyde [338]) or via a physical process (⁶⁰Co irradiation [339]), can further reduce the flammability of PVA/MMT aerogels. Other polysaccharides such as pectin,[340]–[342] chitosan,[343] xanthan gum and agar,[344] or gum Arabic,[345] were also used in combination with mineral fillers to yield fire retardant aerogels. Alginate, alone or with palygorskite,[346] magnesium or aluminum hydroxide, LDH, or Kaolin [347] also showed very good fire behavior with low pHRR at MLC and very high LOI. When combined with MMT and cross-linked with CaCl₂,[347] boron [348] or via pH change [349], they displayed even more impressive behaviors with very low pHRR or no ignition at all.

Interestingly, there is one report on alginate/MMT aerogel used on rigid PUF (RPUF) as fire retardant coating. Alginate/MMT suspension was cast on top of RPUF as 0.2 to 1.5 mm thick coating, and then freeze-dried. A coating made with a formulation of 7.5g of alginate and 7.5g of clay in 100 mL water reduced the pHRR by 30 % with a 0.2 mm coating, and by 60 % with a 1.5 mm coating. Therefore, aerogel coatings require high thickness to be efficient at protecting flammable substrates.

In addition, despite the low flammability of aerogels, their production requires special equipment and procedures which can be expensive. Therefore, drying of hydrogels at ambient condition to produce xerogels is sometimes favored, and for this reason, next part will focus on xerogels.

6.2.4 Xerogels

Xerogels are obtained by drying hydrogels at ambient conditions or elevated temperatures, so that water only evaporates. Although this method is not very common, it is still used to make films and materials from hydrogels. It forms smooth and compact structures. The only

disadvantage is that it can cause severe shrinkage because of the collapse of the pores, but this phenomenon can be controlled. For example, cellulose/MMT plates were made from the hydrogel by hot pressing. LOI values went up to 29 % by increasing MMT content.[350] Nanocomposites with high silica filler content (95 %), in a biomimicry process mimicking nacre composition, were also prepared by air drying a poly(N,N-dimethylacrylamide) composite hydrogel. In this case, air drying was chosen to obtain compact structures and uniform shrinkage. It was introduced in delignified wood porous structure to produce composites, and LOI values over 75% as well as self-extinguishment after exposure to a flame show their high fire retardant potential.[351] As coatings, alginate and alginate/bentonite hydrogels formed via Ca^{2+} cross-linking and air dried also show potential for fire retardancy, although this approach has not been pursued further, to the best of our knowledge. It is reported that while a simple alginate coating could slightly delay the ignition of Masonite supports, gelation significantly increased the time to ignition. The same effect was obtained on balsa wood with the addition of bentonite.[352]

As a conclusion, it is possible to design nanocomposite coatings with high filler contents, just as LbL coatings, but in a one pot procedure thanks to nanoparticles self-assembly. Although it seems a convenient way to bring fire retardancy to flammable substrates, it is way less studied than layer-by-layer coatings. From the literature survey it can be noticed that a crosslinking step brings additional fire retardancy of materials and coatings. Uniformly cross-linked structures can be obtained by synthesizing hydrogels, which can easily incorporate large amount of fillers. Hydrogels have been explored as fire resistant materials for active protection in firefighting. Aerogels are promising fire retardant materials but aerogel fire retardant coatings are difficult to obtain. However, once dried in ambient conditions, hydrogels form thin, compact and smooth structures (xerogels) which are ideal for coating substrates, if the shrinkage is reasonable. Therefore, the combination of high-filler content one pot nanocomposite coatings and gels has great potential for the fire protection of flammable substrates, and could be a viable alternative to step-by-step layer-by-layer coatings.

7. Exploring new opportunities: metallized surfaces as radiative heat barrier.

While pHRR is deemed the most important parameter to look at for improving the fire safety of polymers, one should not overlook the importance of the time to ignition. The short time to ignition of polymers is one of the main reasons they pose such a danger in case of a fire. Having a long time to ignition is a sure way to limit the flame spread and to give more time for people to evacuate the danger zone. Preventing ignition altogether completely suppresses the fire hazard. The ignitability of polymers when subjected to a heat source is enhanced by their low thermal conductivity. Moreover, it is a complex phenomenon which relies on a large number of parameters, one of the most important being heat absorption. In the following parts, it will be demonstrated how thin coatings can help reducing the heat absorption of polymers.

7.1 Heat transfer in fire

During a fire, or in presence of a hot object, heat is transmitted to the surroundings either by conduction, convection or thermal radiation, as the flame behaves as a hot object. The contribution of radiative heat transfer to the total heat flux can be quantified, and this has been the subject of several studies over time. It is acknowledged that in certain conditions, thermal radiations account for a large part of heat transfer in a fire, depending on the scale, fuel type, temperature, ambient oxygen concentration, flame chemistry/composition (notably the presence and type of soot and geometry), etc. It is caused by the absorption (and therefore the emission) of heat from soot. The emission spectrum follows Planck's law, with the addition of the emission of particular infrared wavelength due to the vibration of hot gases such as CO₂. [353] Radiative heat transfer account for a large part of total heat transfer in middle to large scale fires [354] (with a diameter of 0.2 m or more, while convection and conduction dominate at smaller scales). [355], [356]

7.2 Absorption of radiative heat by a material: an optical problem

When a light beam impacts the surface of a material, it will either be reflected or penetrate the object. The fraction of the incident light that is reflected is called reflectance (ρ). Once it penetrates the surface, it is either attenuated or not. In the first case, light is absorbed, in the other case it is transmitted. The fractions of incident energy that are absorbed and transmitted are respectively called absorbance (α) and transmittance (τ). Absorption of light occurs when

the frequency of the incident ray matches the lattice vibration frequency (infrared), or the allowed electronic transitions (UV-visible and Near InfraRed (NIR)) of the material.[357] That is to say, absorption occurs when the material is able to raise its energy level in response to light external stimulation. This is followed by the relaxation of the material back to a more stable state (it lowers its energy level), with emission of a photon. As a consequence, an absorber is also an emitter, and the ratio of its emissive power (its exitance) to the emissive power of a perfect absorber (also called a black body) is the emissivity¹ of the surface. Per definition, it is always inferior to 1, since, theoretically, nothing can absorb and emit more light than a black body.

Additionally, Kirchhoff's law stipulates that, at thermal equilibrium, the power radiated from the surface of a material must be equal to the power absorbed.[358] What follows is that the emissivity of a material is equal to its absorbance: $\varepsilon = \alpha$. For opaque materials, $\tau = 0$, and it follows that: $\varepsilon = 1 - \rho$. Therefore, the emissivity can be linked to the reflectance of a material. The lower the emissivity, the higher the reflectivity, and *vice-versa*. All these quantities are dependent of the wavelength of the incident light, the temperature and direction vector. The terms “spectral” and “directional” will therefore designate one quantity respectively at one distinctive wavelength and direction vector, and the terms total and hemispherical will designate the same quantity integrated over all wavelengths and over a half sphere on top of the surface.

A black body, or any hot object behaving as a black body (the sun, a heated resistance or a sooty fire for example), will absorb and emit all radiation according to Planck's law, which describe the distribution of the intensity of radiation as a function of wavelength:

$$E_b(T, \lambda) = \frac{2\pi h c_0^2}{\lambda^5 [e^{(hc_0/k\lambda T)} - 1]}$$

Integration of this law over all wavelengths will produce the Stefan-Boltzmann law: $E_b(T) = \sigma \cdot T^4$, where k is the Boltzmann constant ($k = 1.3805 \times 10^{-23} \text{ J.K}^{-1}$), h is the Planck constant ($h = 6.6256 \times 10^{-34} \text{ J.s}$), σ is the Stefan-Boltzmann constant ($\sigma = 5.67 \times 10^{-8} \text{ W.m}^{-2}.\text{K}^{-4}$), $c_0 [\text{m.s}^{-1}]$ is

¹According to Modest in Radiative Heat Transfer, the terminology « -ance » is better suited for designating the rough and contaminated surface that this study is concerned about, whereas the terminology “-ivity” is dedicated to pure and smooth materials, as per NIST recommendation. However, as “emissivity” is more commonly used within the scientific community, when compared to “emittance”, we will continue to use this term.

the speed of light in vacuum, and λ [m] is the emission wavelength. Per definition, for a real surface, $E(T,\lambda) = \epsilon \cdot E_b(T,\lambda)$.

When concerned with radiative heat transfer, the wavelengths of interest are comprised between 0.1 μm and 100 μm . They are called thermal radiation and are emitted by any object solely because of its temperature.[359] On the other hand, absorbing them will cause an object to heat up in response, because of induced vibrations. However, by considering a black body as the source of the radiations, for high temperature applications (between 1000 K and 2000 K), heat transfers are controlled by wavelength between 1 and 10 μm , [360] and are governed by the following equation:

$$\Phi = \epsilon \cdot S \cdot \sigma \cdot (T_2^4 - T_1^4)$$

Where Φ is the heat flux between a heat source at temperature T_1 and a surface S with an emissivity ϵ and a temperature T_2 . As infrared radiation is converted into heat at the interface between the environment and the material, it can be considered first as a surface phenomenon.

From this dissertation it can be concluded that lowering the emissivity of the surface of a polymer in the infrared wavelengths can potentially lower its heat absorption and therefore have a huge impact on its ignitability, which has been confirmed recently by numerical simulations.[361]–[364]

7.3 On the use of thin coatings to limit radiative heat transfer

Since limiting heat absorption of polymers is a surface problem, it makes sense to use thin coatings to tackle it. The main applications where this concept has been put into use are the aerospace industry,[365], [366] the military field for infrared stealth,[367]–[369] and energy saving and user comfort in buildings.[370] While the systems can change from one work to another due to several constraints, the core principle remains the same. The coatings are composed of several layers of metals and dielectric. The metal plays the role of a reflector. The other layers either protect it, adjust the reflectivity range to cater for a particular application or promote the adhesion to the substrate.[371] The particularity of such coatings is that they are very thin, usually a few micrometers or even less than one micrometer.

Despite their obvious interest, they have been scarcely applied in fire protection. Paints or composite coatings with infrared reflective pigments [372], [373] have been developed as a first idea to improve flame retardancy of substrates, in order to improve the reflectivity of

conventional white reflective paints in the infrared range. The pigments (aluminum flakes or coated mica flakes) were incorporated in a binder and reflected radiations from 1 to 10 μm specific of a wood fire. TiO_2 particles can also be incorporated but do not reflect the infrared radiation *per se*. They rather scatter the light and therefore must have a specific dimension and concentration.[372]–[374] Their effect was to delay the ignition of wood by a factor of two when exposed to a charcoal fire.[372] Paints containing infrared reflective pigments have been developed for infrared stealth or high temperature applications, but were not tested against any fire scenario.[375], [376] The inconvenience with those types of paints is that the binder can have strong infrared absorption and is usually flammable. An inherently flame retardant binder must therefore be used.[372], [373]

In a recent study, however, Sonnier et al. did develop composites films of polyethylene and aluminum flakes coated on polyethylene substrates. The samples were tested against a standard radiative fire scenario by mass loss cone calorimetry. They found that the time to ignition could be shifted for 80 s to 400 s against a 35 kW/m^2 heat flux.[377]

Applying the same concept of highly infrared reflective coatings as those used in energy savings or aerospace application has however not been pursued in fire protection before the study conducted by Schartel et al. They applied a three layers coating consisting of one chromium adhesive layer, one reflective copper layer, and one silica protective layer, which reached a thickness below 1 μm . [378] The time to ignition was shifted from 58 s to 537 s for a PA66 substrate, while a PC substrate ignited after 459 s of exposure instead of 82 s. This delay was enough to limit the flame spread and fire growth indices, lowering the MAHRE to levels that pass the EN 45545 standard.

Later on, Försth et al reported the use of spectrally selective surface and applied transparent conductive oxide on PMMA. Indium Tin Oxide, because of its electronic conductivity, has a low emissivity. A 0.1 μm coating decreased the absorptivity of PMMA by 30% and shifted its time to ignition from 101 to 257 s at mass loss cone test at 25 kW/m^2 and from 27 to 54 s at 50 kW/m^2 . However, they observed a delamination between the substrate and the ITO coating and stated that the behavior could be improved, should the deposition conditions be optimized. They also coated a steel substrate with VO_2 by gluing the powder with a paint while it was still wet. VO_2 is a thermochromic material which shifts from insulating to conductive (reflective) at high temperature. They only observed a decrease of 5% in the absorptivity in the thermal range of a fire and at the time dismissed the possibility of VO_2 to be used in fire retardant applications.[353] However, in later research they found that by sputtering 50 to 100 nm layers

of VO₂ on glass, the thermal radiation could be reduced by up to 30 %. As they observed a strong absorption starting from 2.7 μm, they concluded that it could not serve a fire retardant purpose by itself, but rather add a welcome side effect to thermochromic windows.[379]

Further studies on this concept have however not been conducted to the best of our knowledge. Low emissivity coatings present therefore a good opportunity for the development of fire protective coatings for flammable substrates.

The authors of these last four studies stated limitations and perspective ideas. First, they observed no effect on the pHRR and THR of the polymeric samples. Then, Sonnier et al. estimated that such coatings would only be effective in a radiative scenario. Against a small flame for example, their protective effect might be lost. Scharrel et al. also proposed that “IR-mirror coatings present the possibility of combination with established flame retardancy approaches to yield the superposition of large effects, in particular combining the flame retardancy against radiation and a small flame”. This was explored in a recent work, where the authors studied the influence of an Al/Al₂O₃ thin coating on the flammability of raw and formulated PA6 and PP substrates. While the protected aluminum coating could shift the time to ignition considerably, it could not alter the combustion behavior of the substrates. But when used in combination with bulk fire retardants for PA6 and PP (respectively, a commercial mixture of melamine polyphosphate and aluminum diethylphosphate, and expandable graphite), the two approaches were found to have a beneficial complementary effect. Against a radiative fire scenario, the low emissivity coating acted first by reflecting infrared rays and preventing heat absorption, which delayed the action of the FR fillers, without impeding their action once it failed.[380]

8. Conclusion

In this review, different kind of fire retardant surface treatments were reported, with an emphasis on thin (nanoscale to microscale) coatings, including plasma, sol-gel and layer-by-layer technologies. Then, different opportunities for the development of new thin coatings were identified and proposed. First, the interest of using one-pot treatments in order to improve the scalability of the research is demonstrated. Indeed, it is one of the challenges of thin flame retardant coatings to have efficient treatments with a small number of steps. Taking into account the self-assembly of nanoparticles could be one of the solutions to have organized architectures such as the one obtained via layer-by-layer processes. Moreover, unconventional treatments and materials were found to have great potential in bringing fire retardancy to a substrate.

Highly cross-linked structures such as dried composite hydrogels could improve the fire behavior of passive composite coatings. Then, impeding radiative heat transfer by casting infrared mirrors on the surface of flammable substrates could greatly improve the flammability, mainly by impeding radiative heat transfer. Some studies have proven the interest of such an approach, as it permits to have time to ignition large enough to reach near incombustibility, however as it is fairly recent, lots of opportunities for improvement remain. Also, fundamental understanding of the mechanisms of protection of fire retardant thin coatings could greatly help the development of new systems, and it should be systematically carried out and supported with quantitative data and extensive characterization.

Other challenges await researchers in the field, the first one being the durability of the treatments. For example, coatings on textile must resist to washing cycles. This is more and more studied in the recent works, and some results were obtained, especially with the use of cross-linked structures or sol-gel technology. However, the durability of the treatments against weathering or fatigue cycles is still scarce and would lack once they are considered for industrial try-outs.

As the regulation becomes more and more restrictive and severe, one must also think about the environmental impact of the treatment. Thin coatings already have an advantage in this effect, as they allow to use less materials and still be effective. Using environmental-friendly processes and materials (clay, natural polysaccharides...) are other leads which are beginning to be well considered by the community.

Another way of improvement is the combination of concepts and approaches. Some thoughts have already been given to it in the literature, for example by combining the fire retardancy of layer-by-layer with the durability of sol-gel, or by using an infrared reflective coating with bulk fire retardants. In some cases, the complementary effects obtained could bring very interesting and original protective features. Especially, this could help reaching protection for a large variety of fire scenario. Diversity of treatments and combination of concepts could also be a solution to the limitations brought by the regulation on fire retardant chemistries.

Finally, one should bear in mind that fire retardancy is a necessary feature of the material, but sometimes not its ultimate purpose. What this statement means is that a fire retardant treatment is sometimes meant only as a protective purpose in the eventual event of a fire, but is not the primary function of the material, especially for upholsteries or textiles. Therefore, the fire retardant surface treatment should be as minimally invasive as possible so as not to impact too

much the functional or esthetical properties of the system, especially mechanical properties. Even more interesting would be multifunctional systems, where several properties (UV or radiation protection, electrical conductivity...) could be met in a single process. This would help the scalability and broaden the application of the proposed treatments.

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Author Contributions

All authors contributed to the discussion and reviewed the manuscript before submission.

Competing interest

The authors declare no competing of interest

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