



HAL
open science

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

Anne-Lise Davesne, Maude Jimenez, Fabienne Samyn, Serge Bourbigot

► To cite this version:

Anne-Lise Davesne, Maude Jimenez, Fabienne Samyn, Serge Bourbigot. Thin coatings for fire protection: An overview of the existing strategies, with an emphasis on layer-by-layer surface treatments and promising new solutions. *Progress in Organic Coatings*, 2021, 154, pp.106217. 10.1016/j.porgcoat.2021.106217 . hal-03163967

HAL Id: hal-03163967

<https://hal.univ-lille.fr/hal-03163967v1>

Submitted on 1 Apr 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Anne-Lise Davesne^a, Maude Jimenez^a, Fabienne Samyn^a, Serge Bourbigot^{a,}*

^aUniv. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France

***Contact:** serge.bourbigot@univ-lille.fr

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.

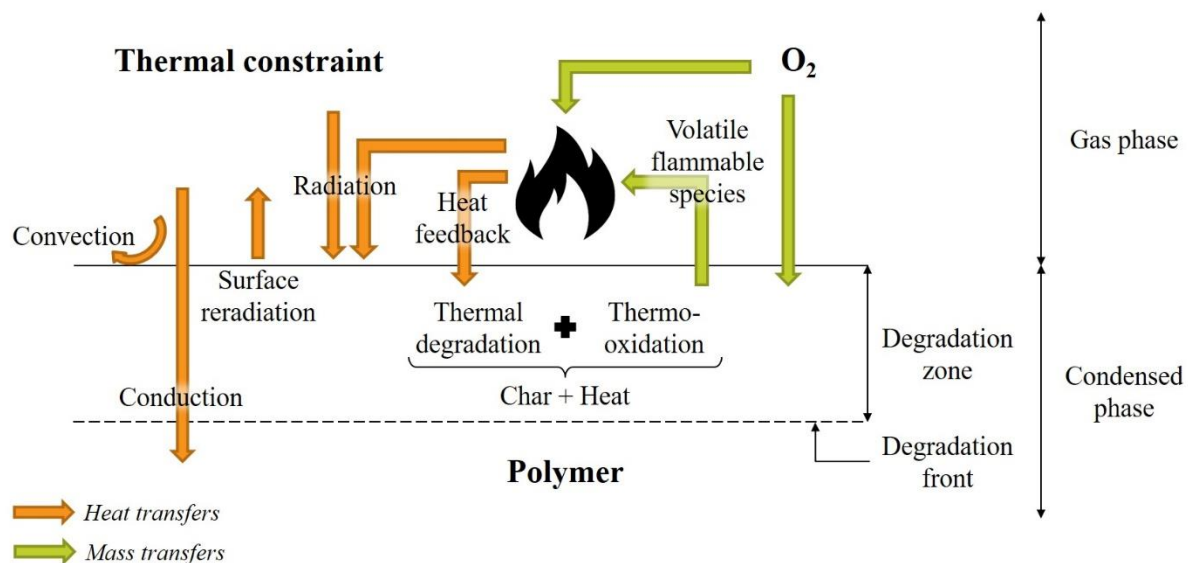


Figure 1. Polymer combustion mechanism.

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]

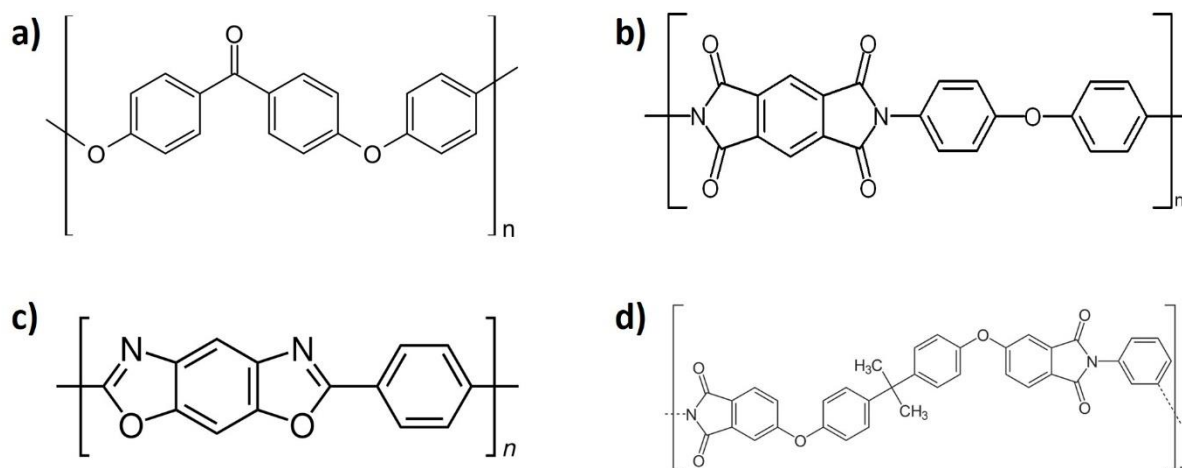


Figure 2. Structures of a) PolyEtherEtherKetone (PEEK), b) an example of PolyImide (PI) commercialized under the name "Kapton", c) PolyBenzOxazole (PBO), commercialized under the name Zylon and d) an example of PolyEther Imide (poly(bisphénol A-co-4-anhydride nitrophthalique-co-1,3-phénylènediamine)).

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]

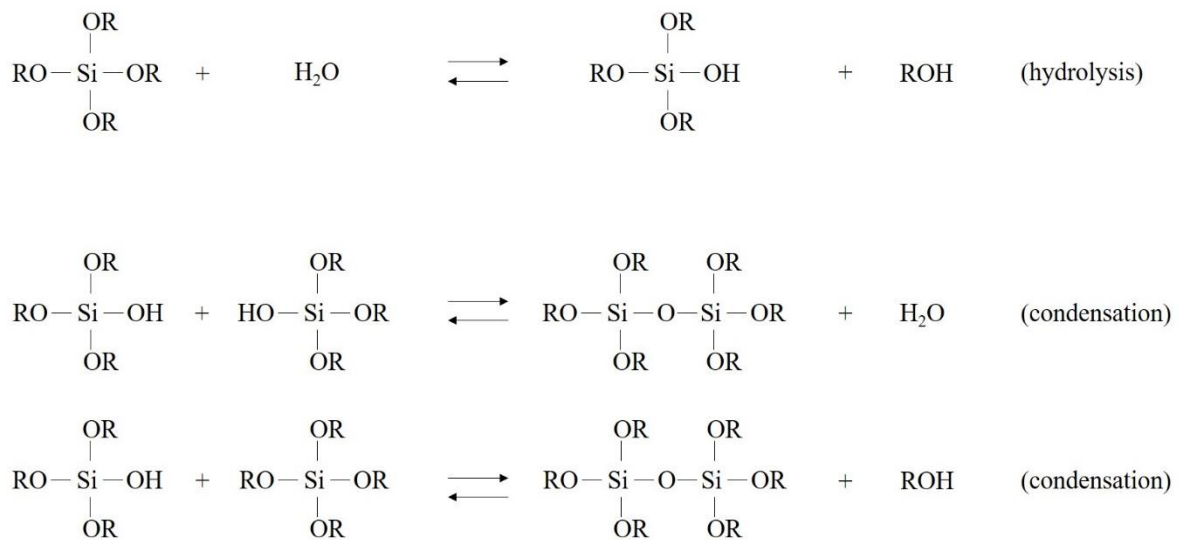


Figure 3. Sol-gel process. (example of silicon alkoxides)

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.

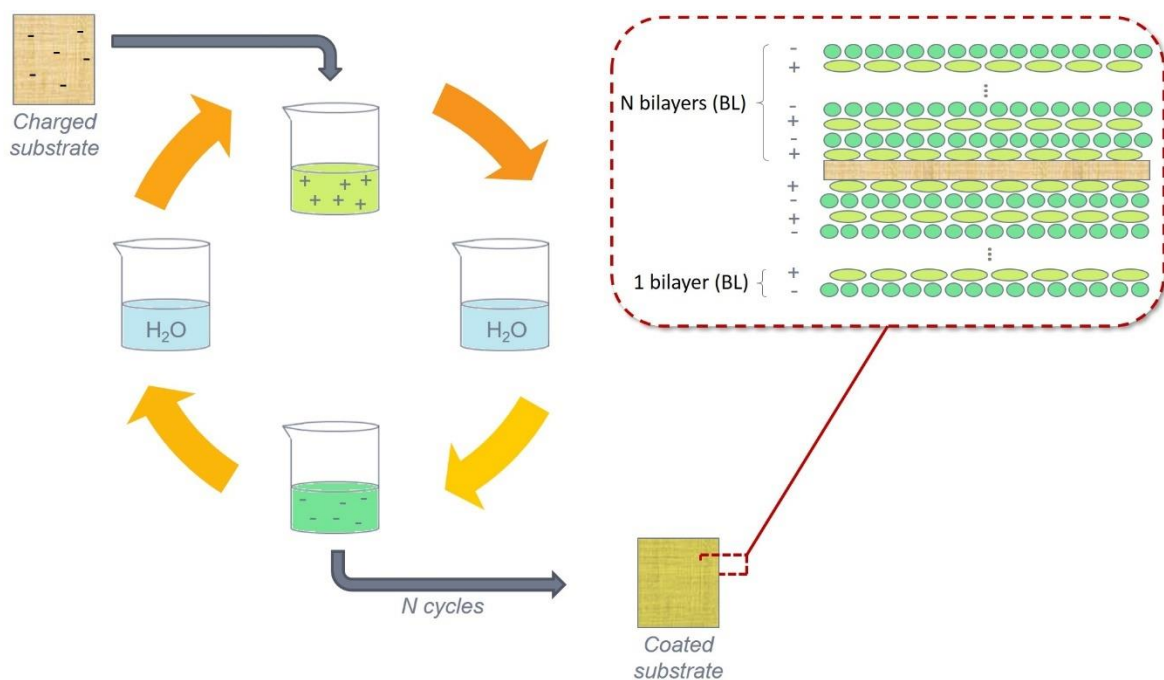


Figure 4. Schematic illustration of the layer-by-layer process (example of electrostatic interaction, with a negatively charged substrate).

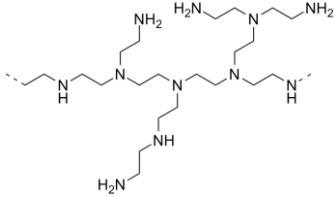
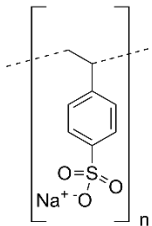
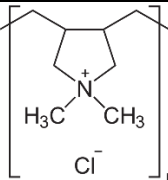
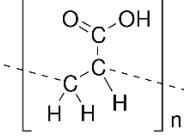
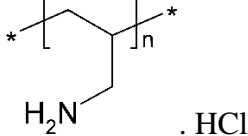
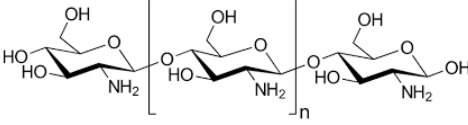
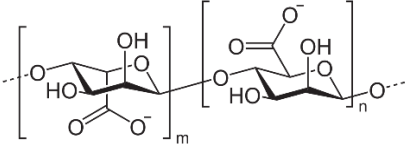
The coating grows from the surface, and the growth profile depends on a lot of parameters. The charge density is important for instance, as well as the ionic force of the solution or the nature of the salt, which can induce more or less screening of the charge, and can cause coiling of polymers' chain, 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.

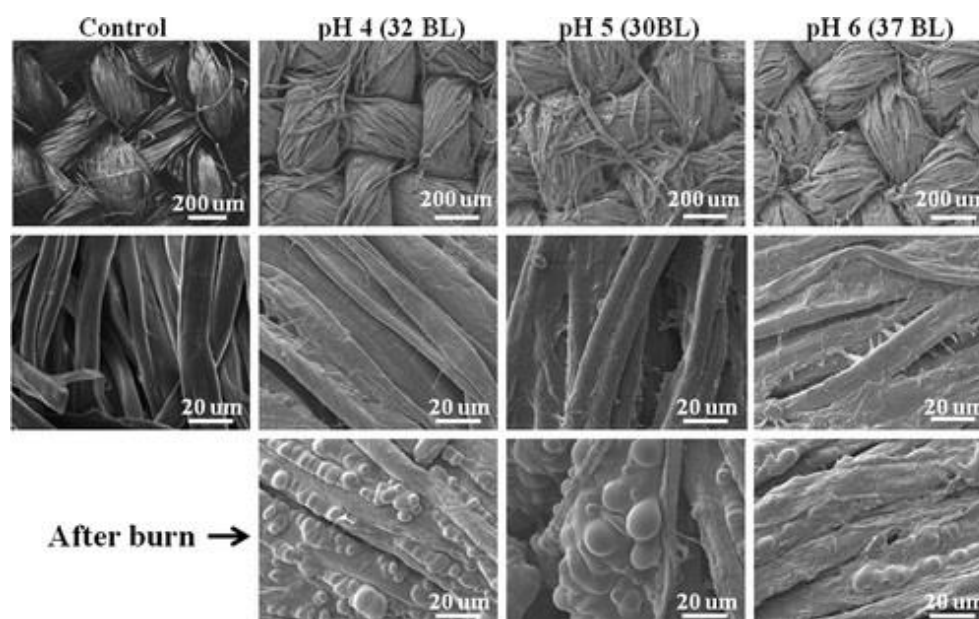


Figure 5. SEM images of coated and uncoated cotton fabric before (top two rows) and after (bottom row) vertical burn testing. The uncoated fabric was completely consumed during burning, so no postburn image can be shown.

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%	[132]
		Poly(allylamine)/MMT + PsP		MLC (60): TTI+96%; pHRR-36%; THR+6%	
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 (H₂O, SO₂, NH₃...) 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%	
		PAA/MMT+PDADMAC/Boehmite +APP/MMT	1	HFT: Self-extinguishment MLC : pHRR-50%; TSR-34%;	[207]
Aerogel	Cellulose nanofibrils	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 Phenoxy-cyclophosphazene 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]

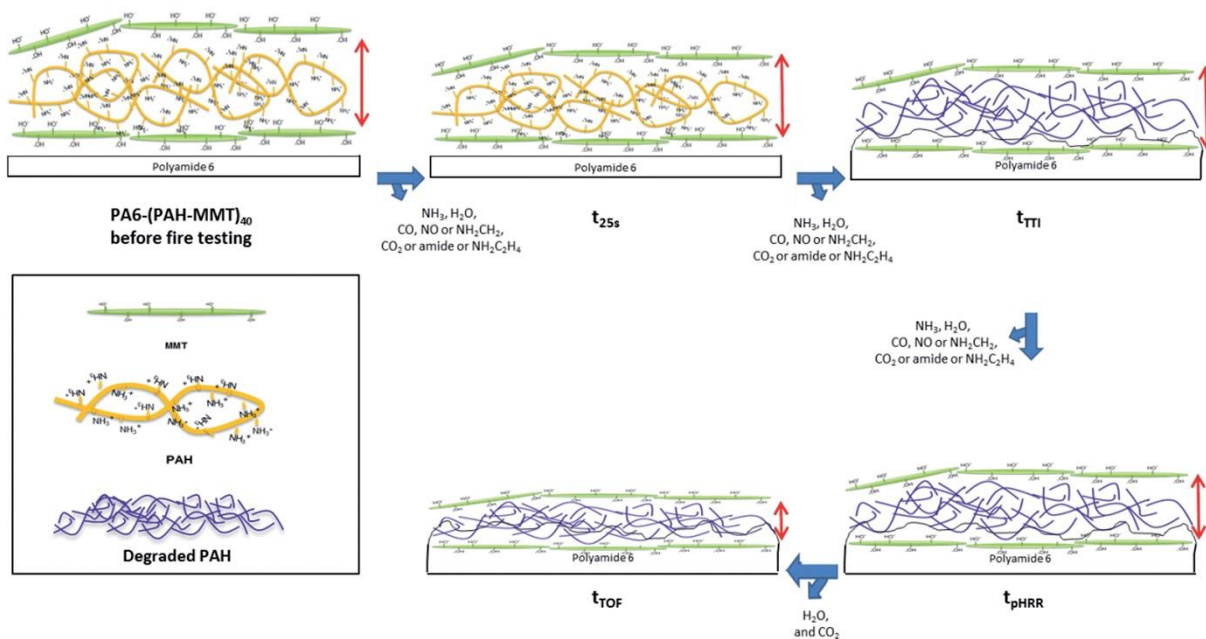


Figure 6. The mechanism of (PAH-MMT)_n flame retardant coating. Reproduced from Ref.[259] with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.

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:

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

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 [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. Schartel 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.

ASSOCIATED CONTENT

Corresponding Author

*Serge Bourbigot (Email: serge.bourbigot@univ-lille.fr)

Author Contributions

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

Competing interest

The authors declare no competing of interest

Acknowledgements

This work was supported by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement n°670647/FireBarConcept/2014-2020).

REFERENCES

- [1] “Les statistiques des Services d’Incendie et de Secours - Edition 2019,” 2019.
- [2] N. N. Brushlinsky, M. Ahrens, S. V. Sokolov, and P. Wagner, “World Fire Statistics 2019,” Paris, France, 2019.
- [3] A. Ramgobin, G. Fontaine, and S. Bourbigot, “Thermal Degradation and Fire Behavior of High Performance Polymers,” *Polym. Rev.*, vol. 59, no. 1, pp. 55–123, Jan. 2019, doi: 10.1080/15583724.2018.1546736.

- [4] S. Bourbigot and S. Duquesne, “Fire retardant polymers: Recent developments and opportunities,” *J. Mater. Chem.*, vol. 17, no. 22, pp. 2283–2300, 2007, doi: 10.1039/b702511d.
- [5] H. Ge, W. Wang, Y. Pan, X. Yu, W. Hu, and Y. Hu, “An inherently flame-retardant polyamide containing a phosphorus pendent group prepared by interfacial polymerization,” *RSC Adv.*, vol. 6, no. 85, pp. 81802–81808, 2016, doi: 10.1039/c6ra17108g.
- [6] W. Hu *et al.*, “Flame retardant polystyrene copolymers: Preparation, thermal properties, and fire toxicities,” *Polym. Adv. Technol.*, vol. 25, no. 6, pp. 631–637, 2014, doi: 10.1002/pat.3261.
- [7] A. B. Morgan and A. Z. Worku, *Flame Retardants: Overview*. 2015.
- [8] A. B. Morgan, “The Future of Flame Retardant Polymers—Unmet Needs and Likely New Approaches,” *Polym. Rev.*, vol. 59, no. 1, pp. 25–54, 2019, doi: 10.1080/15583724.2018.1454948.
- [9] S. Bourbigot and S. Duquesne, “Intumescence and Nanocomposites: A Novel Route for Flame-Retarding Polymeric Materials,” in *Flame Retardant Polymer Nanocomposites*, A. B. Morgan and C. A. Wilkie, Eds. John Wiley & Sons, Inc., 2006, pp. 131–162.
- [10] S. Liang, N. M. Neisius, and S. Gaan, “Recent developments in flame retardant polymeric coatings,” *Prog. Org. Coatings*, vol. 76, no. 11, pp. 1642–1665, 2013, doi: 10.1016/j.porgcoat.2013.07.014.
- [11] S. T. Lazar, T. J. Kolibaba, and J. C. Grunlan, “Flame-retardant surface treatments,” *Nat. Rev. Mater.*, vol. 5, no. 4, pp. 259–275, 2020, doi: 10.1038/s41578-019-0164-6.
- [12] H. Dislich and P. Hinz, “History and principles of the sol-gel process, and some new multicomponent oxide coatings,” *J. Non. Cryst. Solids*, vol. 48, no. 1, pp. 11–16, 1982, doi: 10.1016/0022-3093(82)90242-3.
- [13] U. Schubert, “Chemistry and Fundamentals of the Sol-Gel Process,” in *The Sol-Gel Handbook: Synthesis, Characterization, and Applications*, 1st ed., D. Levy and M. Zayat, Eds. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2015, pp. 1–28.

- [14] J. Livage, "Basic Principles of Sol-Gel Chemistry," in *Sol-Gel Technologies for Glass Producers and Users*, M. A. Aegerter and M. Mennig, Eds. Boston, MA: Springer US, 2004, pp. 3–14.
- [15] S. Karataş, Z. Hoşgör, Y. Menceloğlu, N. Kayaman-Apohan, and A. Güngör, "Synthesis and characterization of flame retarding UV-curable organic–inorganic hybrid coatings," *J. Appl. Polym. Sci.*, vol. 102, no. 2, pp. 1906–1914, Oct. 2006, doi: 10.1002/app.24274.
- [16] S. Karataş, N. Kayaman-Apohan, O. Turunç, and A. Güngör, "Synthesis and characterization of UV-curable phosphorus containing hybrid materials prepared by sol-gel technique," *Polym. Adv. Technol.*, vol. 22, no. 5, pp. 567–576, May 2011, doi: 10.1002/pat.1546.
- [17] C. Kizilkaya, S. Karataş, N. K. Apohan, and A. Güngör, "Synthesis and characterization of novel polyimide/SiO₂ nanocomposite materials containing phenylphosphine oxide via sol-gel technique," *Journal of Applied Polymer Science*, vol. 115, no. 6, pp. 3256–3264, 2010, doi: 10.1002/app.31404.
- [18] Y. Mülazim, M. V. Kahraman, N. K. Apohan, S. Kiziltaş, and A. Güngör, "Preparation and characterization of UV-curable, boron-containing, transparent hybrid coatings," *Journal of Applied Polymer Science*, vol. 120, no. 4, pp. 2112–2121, 2011, doi: 10.1002/app.33358.
- [19] Y. Mülazim, E. Çakmakçı, and M. V. Kahraman, "Preparation of photo curable highly hydrophobic coatings using a modified castor oil derivative as a sol-gel component," *Prog. Org. Coatings*, vol. 72, no. 3, pp. 394–401, 2011, doi: 10.1016/j.porgcoat.2011.05.012.
- [20] E. Baştürk, B. Oktay, M. V. Kahraman, and N. Kayaman Apohan, "UV cured thiol-ene flame retardant hybrid coatings," *Prog. Org. Coatings*, vol. 76, no. 6, pp. 936–943, 2013, doi: 10.1016/j.porgcoat.2012.10.012.
- [21] D. Shang, X. Sun, J. Hang, L. Jin, and L. Shi, "Flame resistance, physical and mechanical properties of UV-cured hybrid coatings containing low-hydroxyl-content sols via an anhydrous sol-gel process," *Prog. Org. Coatings*, vol. 105, pp. 267–276, 2017, doi: 10.1016/j.porgcoat.2017.01.015.

- [22] M. Messoria *et al.*, “Flame retarding poly(methyl methacrylate) with nanostructured organic-inorganic hybrids coatings,” *Polymer (Guildf)*., vol. 44, no. 16, pp. 4463–4470, 2003, doi: 10.1016/S0032-3861(03)00396-3.
- [23] K. Satoh, H. Nakazumi, and M. Morita, “Novel Fluorinated Inorganic-Organic Finishing Materials for Nylon Carpeting,” *Text. Res. J.*, vol. 74, no. 12, pp. 1079–1084, 2004, doi: 10.1177/004051750407401209.
- [24] S. Bellayer, M. Jimenez, S. Barrau, and S. Bourbigot, “Fire retardant sol–gel coatings for flexible polyurethane foams,” *RSC Adv.*, vol. 6, no. 34, pp. 28543–28554, 2016, doi: 10.1039/C6RA02094A.
- [25] Z. M. Zhu, Y. J. Xu, W. Liao, S. Xu, and Y. Z. Wang, “Highly Flame Retardant Expanded Polystyrene Foams from Phosphorus-Nitrogen-Silicon Synergistic Adhesives,” *Ind. Eng. Chem. Res.*, vol. 56, no. 16, pp. 4649–4658, 2017, doi: 10.1021/acs.iecr.6b05065.
- [26] E. Baştürk, T. Inan, and A. Güngör, “Flame retardant UV-curable acrylated epoxidized soybean oil based organic-inorganic hybrid coating,” *Prog. Org. Coatings*, vol. 76, no. 6, pp. 985–992, 2013, doi: 10.1016/j.porgcoat.2012.10.007.
- [27] F. Girardi *et al.*, “Hybrid organic-inorganic materials as coatings for protecting wood,” *Prog. Org. Coatings*, vol. 77, no. 2, pp. 449–457, 2014, doi: 10.1016/j.porgcoat.2013.11.010.
- [28] J. Alongi and G. Malucelli, “Cotton fabrics treated with novel oxidic phases acting as effective smoke suppressants,” *Carbohydr. Polym.*, vol. 90, no. 1, pp. 251–260, 2012, doi: 10.1016/j.carbpol.2012.05.032.
- [29] J. Alongi, M. Ciobanu, and G. Malucelli, “Sol-gel treatments for enhancing flame retardancy and thermal stability of cotton fabrics: Optimisation of the process and evaluation of the durability,” *Cellulose*, vol. 18, no. 1, pp. 167–177, 2011, doi: 10.1007/s10570-010-9470-2.
- [30] J. Alongi, M. Ciobanu, and G. Malucelli, “Sol-gel treatments on cotton fabrics for improving thermal and flame stability: Effect of the structure of the alkoxy silane precursor,” *Carbohydr. Polym.*, vol. 87, no. 1, pp. 627–635, 2012, doi: 10.1016/j.carbpol.2011.08.036.

- [31] J. Alongi, M. Ciobanu, and G. Malucelli, "Cotton fabrics treated with hybrid organic-inorganic coatings obtained through dual-cure processes," *Cellulose*, vol. 18, no. 5, pp. 1335–1348, 2011, doi: 10.1007/s10570-011-9564-5.
- [32] C. Colleoni, I. Donelli, G. Freddi, E. Guido, V. Migani, and G. Rosace, "A novel sol-gel multi-layer approach for cotton fabric finishing by tetraethoxysilane precursor," *Surf. Coatings Technol.*, vol. 235, pp. 192–203, 2013, doi: 10.1016/j.surfcoat.2013.07.033.
- [33] G. Brancatelli, C. Colleoni, M. R. Massafra, and G. Rosace, "Effect of hybrid phosphorus-doped silica thin films produced by sol-gel method on the thermal behavior of cotton fabrics," *Polym. Degrad. Stab.*, vol. 96, no. 4, pp. 483–490, 2011, doi: 10.1016/j.polymdegradstab.2011.01.013.
- [34] S. Deh, F. Gähr, and M. R. Buchmeiser, "Synergistic effects in the pyrolysis of phosphorus-based flame-retardants: The role of Si- and N-based compounds," *Polym. Degrad. Stab.*, vol. 130, pp. 155–164, 2016, doi: 10.1016/j.polymdegradstab.2016.06.009.
- [35] V. Rajendran, N. R. Dhineshabu, R. R. Kanna, and K. V. I. S. Kaler, "Enhancement of thermal stability, flame retardancy, and antimicrobial properties of cotton fabrics functionalized by inorganic nanocomposites," *Ind. Eng. Chem. Res.*, vol. 53, no. 50, pp. 19512–19524, 2014, doi: 10.1021/ie502584m.
- [36] R. S. Kappes, T. Urbainczyk, U. Artz, T. Textor, and J. S. Gutmann, "Flame retardants based on amino silanes and phenylphosphonic acid," *Polym. Degrad. Stab.*, vol. 129, pp. 168–179, 2016, doi: 10.1016/j.polymdegradstab.2016.04.012.
- [37] J. Alongi, M. Ciobanu, and G. Malucelli, "Thermal stability, flame retardancy and mechanical properties of cotton fabrics treated with inorganic coatings synthesized through sol-gel processes," *Carbohydr. Polym.*, vol. 87, no. 3, pp. 2093–2099, 2012, doi: 10.1016/j.carbpol.2011.10.032.
- [38] J. Alongi, M. Ciobanu, J. Tata, F. Carosio, and G. Malucelli, "Thermal stability and flame retardancy of polyester, cotton, and relative blend textile fabrics subjected to sol-gel treatments," *J. Appl. Polym. Sci.*, vol. 119, no. 4, pp. 1961–1969, Feb. 2011, doi: 10.1002/app.32954.

- [39] C. K. Kundu, X. Wang, Y. Hou, and Y. Hu, "Construction of flame retardant coating on polyamide 6.6 via UV grafting of phosphorylated chitosan and sol-gel process of organo-silane," *Carbohydr. Polym.*, vol. 181, no. November 2017, pp. 833–840, 2018, doi: 10.1016/j.carbpol.2017.11.069.
- [40] E. Guido *et al.*, "Thermal stability and flame retardancy of polyester fabrics sol-gel treated in the presence of boehmite nanoparticles," *Polym. Degrad. Stab.*, vol. 98, no. 9, pp. 1609–1616, 2013, doi: 10.1016/j.polymdegradstab.2013.06.021.
- [41] C. K. Kundu, X. Wang, L. Liu, L. Song, and Y. Hu, "Few layer deposition and sol-gel finishing of organic-inorganic compounds for improved flame retardant and hydrophilic properties of polyamide 66 textiles: A hybrid approach," *Prog. Org. Coatings*, vol. 129, no. November 2018, pp. 318–326, 2019, doi: 10.1016/j.porgcoat.2019.01.010.
- [42] J. Alongi, C. Colleoni, G. Malucelli, and G. Rosace, "Hybrid phosphorus-doped silica architectures derived from a multistep sol-gel process for improving thermal stability and flame retardancy of cotton fabrics," *Polym. Degrad. Stab.*, vol. 97, no. 8, pp. 1334–1344, 2012, doi: 10.1016/j.polymdegradstab.2012.05.030.
- [43] J. Alongi, C. Colleoni, G. Rosace, and G. Malucelli, "The role of pre-hydrolysis on multi step sol-gel processes for enhancing the flame retardancy of cotton," *Cellulose*, vol. 20, no. 1, pp. 525–535, 2013, doi: 10.1007/s10570-012-9806-1.
- [44] J. Alongi, C. Colleoni, G. Rosace, and G. Malucelli, "Sol-gel derived architectures for enhancing cotton flame retardancy: Effect of pure and phosphorus-doped silica phases," *Polym. Degrad. Stab.*, vol. 99, no. 1, pp. 92–98, 2014, doi: 10.1016/j.polymdegradstab.2013.11.020.
- [45] J. Alongi, C. Colleoni, G. Rosace, and G. Malucelli, "Phosphorus- and nitrogen-doped silica coatings for enhancing the flame retardancy of cotton: Synergisms or additive effects?," *Polym. Degrad. Stab.*, vol. 98, no. 2, pp. 579–589, 2013, doi: 10.1016/j.polymdegradstab.2012.11.017.
- [46] J. Alongi, M. Ciobanu, and G. Malucelli, "Novel flame retardant finishing systems for cotton fabrics based on phosphorus-containing compounds and silica derived from sol-gel processes," *Carbohydr. Polym.*, vol. 85, no. 3, pp. 599–608, 2011, doi: 10.1016/j.carbpol.2011.03.024.

- [47] F. Samyn, M. Vandewalle, S. Bellayer, and S. Duquesne, "Sol-gel treatments to flame retard PA11/flax composites," *Fibers*, vol. 7, no. 10, 2019, doi: 10.3390/fib7100086.
- [48] X. W. Cheng, R. C. Tang, J. P. Guan, and S. Q. Zhou, "An eco-friendly and effective flame retardant coating for cotton fabric based on phytic acid doped silica sol approach," *Prog. Org. Coatings*, vol. 141, no. January, p. 105539, 2020, doi: 10.1016/j.porgcoat.2020.105539.
- [49] Y. Ren, Y. Zhang, Y. Gu, and Q. Zeng, "Flame retardant polyacrylonitrile fabrics prepared by organic-inorganic hybrid silica coating via sol-gel technique," *Prog. Org. Coatings*, vol. 112, no. August, pp. 225–233, 2017, doi: 10.1016/j.porgcoat.2017.07.022.
- [50] M. Barbalini, L. Bertolla, J. Toušek, and G. Malucelli, "Hybrid silica-phytic acid coatings: Effect on the thermal stability and flame retardancy of cotton," *Polymers (Basel)*, vol. 11, no. 10, 2019, doi: 10.3390/polym11101664.
- [51] D. Zhang *et al.*, "Flame retardant and hydrophobic coatings on cotton fabrics via sol-gel and self-assembly techniques," *J. Colloid Interface Sci.*, vol. 505, pp. 892–899, 2017, doi: 10.1016/j.jcis.2017.06.087.
- [52] D. Lin, X. Zeng, H. Li, X. Lai, and T. Wu, "One-pot fabrication of superhydrophobic and flame-retardant coatings on cotton fabrics via sol-gel reaction," *J. Colloid Interface Sci.*, vol. 533, pp. 198–206, 2019, doi: 10.1016/j.jcis.2018.08.060.
- [53] H. Nabipour, X. Wang, L. Song, and Y. Hu, "Hydrophobic and flame-retardant finishing of cotton fabrics for water–oil separation," *Cellulose*, vol. 27, no. 7, pp. 4145–4159, 2020, doi: 10.1007/s10570-020-03057-1.
- [54] Y. Liu *et al.*, "Effect of phosphorus-containing inorganic-organic hybrid coating on the flammability of cotton fabrics: Synthesis, characterization and flammability," *Chem. Eng. J.*, vol. 294, pp. 167–175, 2016, doi: 10.1016/j.cej.2016.02.080.
- [55] Y. S. Zhu, F. You, H. T. Zhou, W. H. Huangfu, and Z. H. Wang, "Pyrolysis Properties and Flame Retardant Effects of Fabrics Finished by Hybrid Silica-based Sols," *Procedia Eng.*, vol. 211, pp. 1091–1101, 2018, doi: 10.1016/j.proeng.2017.12.114.
- [56] J. Vasiljević *et al.*, "Functionalization of cellulose fibres with DOPO-polysilsesquioxane flame retardant nanocoating," *Cellulose*, vol. 22, no. 3, pp. 1893–1910, 2015, doi: 10.1007/s10570-015-0599-x.

- [57] J. Vasiljević *et al.*, “Study of flame-retardant finishing of cellulose fibres: Organic-inorganic hybrid versus conventional organophosphonate,” *Polym. Degrad. Stab.*, vol. 98, no. 12, pp. 2602–2608, 2013, doi: 10.1016/j.polymdegradstab.2013.09.020.
- [58] A. M. Grancaric, C. Colleoni, E. Guido, L. Botteri, and G. Rosace, “Thermal behaviour and flame retardancy of monoethanolamine-doped sol-gel coatings of cotton fabric,” *Prog. Org. Coatings*, vol. 103, pp. 174–181, 2017, doi: 10.1016/j.porgcoat.2016.10.035.
- [59] Z. Jiang, D. Xu, X. Ma, J. Liu, and P. Zhu, “Facile synthesis of novel reactive phosphoramidate siloxane and application to flame retardant cellulose fabrics,” *Cellulose*, vol. 26, no. 9, pp. 5783–5796, 2019, doi: 10.1007/s10570-019-02465-2.
- [60] J. Alongi and G. Malucelli, “Thermal stability, flame retardancy and abrasion resistance of cotton and cotton-linen blends treated by sol-gel silica coatings containing alumina micro- or nano-particles,” *Polym. Degrad. Stab.*, vol. 98, no. 8, pp. 1428–1438, 2013, doi: 10.1016/j.polymdegradstab.2013.05.002.
- [61] M. H. Fallah, S. A. Fallah, and M. A. Zanjanchi, “Synthesis and characterization of nano-sized zinc oxide coating on cellulosic fibers: Photoactivity and flame-retardancy study,” *Chinese J. Chem.*, vol. 29, no. 6, pp. 1239–1245, 2011, doi: 10.1002/cjoc.201190230.
- [62] Q. hua Zhang, J. Gu, G. qiang Chen, and T. ling Xing, “Durable flame retardant finish for silk fabric using boron hybrid silica sol,” *Appl. Surf. Sci.*, vol. 387, pp. 446–453, 2016, doi: 10.1016/j.apsusc.2016.06.119.
- [63] Q. Zhang *et al.*, “Flame retardance and thermal stability of wool fabric treated by boron containing silica sols,” *Mater. Des.*, vol. 85, pp. 796–799, 2015, doi: 10.1016/j.matdes.2015.07.163.
- [64] A. Šehić, B. Tomšič, I. Jerman, J. Vasiljević, J. Medved, and B. Simončič, “Synergistic inhibitory action of P- and Si-containing precursors in sol-gel coatings on the thermal degradation of polyamide 6,” *Polym. Degrad. Stab.*, vol. 128, pp. 245–252, 2016, doi: 10.1016/j.polymdegradstab.2016.03.026.
- [65] A. A. Younis, “Optimization of mechanical, thermal, and ignition properties of polyester fabric using urea and phosphoric acid,” *J. Ind. Text.*, vol. 49, no. 6, pp. 791–808, 2020, doi: 10.1177/1528083718798636.

- [66] A. Quédé *et al.*, “Elaboration of fire retardant coatings on polyamide-6 using a cold plasma polymerization process,” *Surf. Coatings Technol.*, vol. 151–152, pp. 424–428, 2002, doi: 10.1016/S0257-8972(01)01646-2.
- [67] A. Quédé *et al.*, “Thermal stability and flammability studies of coated polymer powders using a plasma fluidized bed process,” *J. Mater. Sci.*, vol. 37, no. 7, pp. 1395–1399, 2002, doi: 10.1023/A:1014576730732.
- [68] S. Bourbigot, C. Jama, M. Le Bras, R. Delobel, O. Dessaux, and P. Goudmand, “New approach to flame retardancy using plasma assisted surface polymerisation techniques,” *Polym. Degrad. Stab.*, vol. 66, no. 1, pp. 153–155, 1999, doi: 10.1016/S0141-3910(99)00059-2.
- [69] C. Jama *et al.*, “Fire Retardancy and Thermal Stability of Materials Coated by Organosilicon Thin Films Using a Cold Remote Plasma Process,” pp. 200–213, 2001, doi: 10.1021/bk-2001-0797.ch016.
- [70] J. Bardon *et al.*, “Characterization of a plasma polymer coating from an organophosphorus silane deposited at atmospheric pressure for fire-retardant purposes,” *Prog. Org. Coatings*, vol. 88, pp. 39–47, 2015, doi: 10.1016/j.porgcoat.2015.06.005.
- [71] B. Schartel, G. Kühn, R. Mix, and J. Friedrich, “Surface controlled fire retardancy of polymers using plasma polymerisation,” *Macromol. Mater. Eng.*, vol. 287, no. 9, pp. 579–582, 2002, doi: 10.1002/1439-2054(20020901)287:9<579::AID-MAME579>3.0.CO;2-6.
- [72] F. Hilt, N. Gherardi, D. Duday, A. Berné, and P. Choquet, “Efficient Flame Retardant Thin Films Synthesized by Atmospheric Pressure PECVD through the High Co-deposition Rate of Hexamethyldisiloxane and Triethylphosphate on Polycarbonate and Polyamide-6 Substrates,” *ACS Appl. Mater. Interfaces*, vol. 8, no. 19, pp. 12422–12433, May 2016, doi: 10.1021/acsami.6b01819.
- [73] J. Li, W. Tong, and L. Yi, “Flame-retardant composite coatings for cotton fabrics fabricated by using oxygen plasma-induced polymerization of vinyl phosphonic acid/cyclotetrasiloxane,” *Text. Res. J.*, vol. 89, no. 23–24, pp. 5053–5066, 2019, doi: 10.1177/0040517519848158.

- [74] A. R. Horrocks, S. Nazaré, R. Masood, B. Kandola, and D. Price, “Surface modification of fabrics for improved flash-fire resistance using atmospheric pressure plasma in the presence of a functionalized clay and polysiloxane,” *Polymers for Advanced Technologies*, vol. 22, no. 1, pp. 22–29, 2011, doi: 10.1002/pat.1707.
- [75] A. Quédé, B. Mutel, P. Supiot, C. Jama, O. Dessaux, and R. Delobel, “Characterization of organosilicon films synthesized by N₂-PACVD. Application to fire retardant properties of coated polymers,” *Surf. Coatings Technol.*, vol. 180–181, pp. 265–270, 2004, doi: 10.1016/j.surfcoat.2003.10.067.
- [76] M. J. Tsafack and J. Levalois-Grützmacher, “Plasma-induced graft-polymerization of flame retardant monomers onto PAN fabrics,” *Surf. Coatings Technol.*, vol. 200, no. 11, pp. 3503–3510, 2006, doi: 10.1016/j.surfcoat.2004.11.030.
- [77] M. J. Tsafack and J. Levalois-Grützmacher, “Towards multifunctional surfaces using the plasma-induced graft-polymerization (PIGP) process: Flame and waterproof cotton textiles,” *Surf. Coatings Technol.*, vol. 201, no. 12, pp. 5789–5795, 2007, doi: 10.1016/j.surfcoat.2006.10.027.
- [78] B. Paosawatyanong, P. Jermsutjarit, and W. Bhanthumnavin, “Graft copolymerization coating of methacryloyloxyethyl diphenyl phosphate flame retardant onto silk surface,” *Prog. Org. Coatings*, vol. 77, no. 10, pp. 1585–1590, 2014, doi: 10.1016/j.porgcoat.2014.01.023.
- [79] K. Kamlangkla, S. K. Hodak, and J. Levalois-Grützmacher, “Multifunctional silk fabrics by means of the plasma induced graft polymerization (PIGP) process,” *Surf. Coatings Technol.*, vol. 205, no. 13–14, pp. 3755–3762, 2011, doi: 10.1016/j.surfcoat.2011.01.006.
- [80] S. Zanini, C. Riccardi, M. Orlandi, C. Colombo, and F. Croccolo, “Plasma-induced graft-polymerisation of ethylene glycol methacrylate phosphate on polyethylene films,” *Polym. Degrad. Stab.*, vol. 93, no. 6, pp. 1158–1163, 2008, doi: 10.1016/j.polymdegradstab.2008.03.009.
- [81] H. Yavuz, Z. Rzaev, and N. Dilsiz, “Characterisation of flame retardant plasma polymer deposited BOPP film,” *Plast. Rubber Compos.*, vol. 37, no. 5–6, pp. 268–275, 2008, doi: 10.1179/174328908X309385.

- [82] I. Errifai *et al.*, “Elaboration of a fire retardant coating for polyamide-6 using cold plasma polymerization of a fluorinated acrylate,” *Surf. Coatings Technol.*, vol. 180–181, pp. 297–301, 2004, doi: 10.1016/j.surfcoat.2003.10.074.
- [83] F. Carosio, J. Alongi, and A. Frache, “Influence of surface activation by plasma and nanoparticle adsorption on the morphology, thermal stability and combustion behavior of PET fabrics,” *Eur. Polym. J.*, vol. 47, no. 5, pp. 893–902, 2011, doi: 10.1016/j.eurpolymj.2011.01.009.
- [84] B. K. Kandola and P. Luangtriratana, “Thermo-physical performance of organoclay coatings deposited on the surfaces of glass fibre-reinforced epoxy composites using an atmospheric pressure plasma or a resin binder,” *Appl. Clay Sci.*, vol. 99, pp. 62–71, 2014, doi: 10.1016/j.clay.2014.06.013.
- [85] Z. Ömeroğulları and D. Kut, “Application of low-frequency oxygen plasma treatment to polyester fabric to reduce the amount of flame retardant agent,” *Text. Res. J.*, vol. 82, no. 6, pp. 613–621, 2012, doi: 10.1177/0040517511420758.
- [86] Z. R. Farag, S. Krüger, G. Hidde, A. Schimanski, C. Jäger, and J. Friedrich, “Deposition of thick polymer or inorganic layers with flame-retardant properties by combination of plasma and spray processes,” *Surf. Coatings Technol.*, vol. 228, pp. 266–274, 2013, doi: 10.1016/j.surfcoat.2013.04.039.
- [87] V. Totolin, M. Sarmadi, S. O. Manolache, and F. S. Denes, “Environmentally friendly flame-retardant materials produced by atmospheric pressure plasma modifications,” *J. Appl. Polym. Sci.*, vol. 124, no. 1, pp. 116–122, Apr. 2012, doi: 10.1002/app.35087.
- [88] V. Totolin, M. Sarmadi, S. O. Manolache, and F. S. Denes, “Atmospheric pressure plasma enhanced synthesis of flame retardant cellulosic materials,” *J. Appl. Polym. Sci.*, vol. 117, no. 5, pp. 281–289, 2010, doi: 10.1002/app.31987.
- [89] G. Decher, J. D. Hong, and J. Schmitt, “Buildup of ultrathin multilayer films by a self-assembly process: III. Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces,” *Thin Solid Films*, vol. 210–211, no. PART 2, pp. 831–835, 1992, doi: 10.1016/0040-6090(92)90417-A.
- [90] G. Decher, “Layer-by-Layer Assembly (Putting Molecules to Work),” *Multilayer Thin Film. Seq. Assem. Nanocomposite Mater. Second Ed.*, vol. 1, pp. 1–21, 2012, doi: 10.1002/9783527646746.ch1.

- [91] R. K. Iler, "Multilayers of colloidal particles," *J. Colloid Interface Sci.*, vol. 21, no. 6, pp. 569–594, 1966.
- [92] J. M. Lehn, "Towards complex matter: Supramolecular chemistry and self-organization," *Eur. Rev.*, vol. 17, no. 2, pp. 263–280, 2009, doi: 10.1017/S1062798709000805.
- [93] G. M. Whitesides, J. P. Mathias, and C. T. Seto, "Molecular self-assembly and nanochemistry: A chemical strategy for the synthesis of nanostructures," *Science (80-.)*, vol. 254, no. 5036, pp. 1312–1319, 1991, doi: 10.1126/science.1962191.
- [94] R. S. Tu and M. Tirrell, "Bottom-up design of biomimetic assemblies," *Adv. Drug Deliv. Rev.*, vol. 56, no. 11, pp. 1537–1563, 2004, doi: 10.1016/j.addr.2003.10.047.
- [95] R. Mérindol, "Layer-by-layer assembly of strong bio-inspired nanocomposites," Université de Strasbourg, 2014.
- [96] P. Lavalle *et al.*, "Comparison of the structure of polyelectrolyte multilayer films exhibiting a linear and an exponential growth regime: An in situ atomic force microscopy study," *Macromolecules*, vol. 35, no. 11, pp. 4458–4465, 2002, doi: 10.1021/ma0119833.
- [97] P. Podsiadlo *et al.*, "Exponential growth of LBL films with incorporated inorganic sheets," *Nano Lett.*, vol. 8, no. 6, pp. 1762–1770, 2008, doi: 10.1021/nl8011648.
- [98] X. Li, P. Fan, X. Tuo, Y. He, and X. Wang, "Photoresponsive layer-by-layer ultrathin films prepared from a hyperbranched azobenzene-containing polymeric diazonium salt," *Thin Solid Films*, vol. 517, no. 6, pp. 2055–2062, 2009, doi: 10.1016/j.tsf.2008.10.136.
- [99] K. Araki, M. J. Wagner, and M. S. Wrighton, "Layer-by-layer growth of electrostatically assembled multilayer porphyrin films," *Langmuir*, vol. 12, no. 22, pp. 5393–5398, 1996, doi: 10.1021/la960024c.
- [100] A. Martin *et al.*, "Controlled release of encapsulated methylene blue in a multilayered textile coating," *MATEC Web Conf.*, vol. 7, 2013, doi: 10.1051/mateconf/20130704012.
- [101] S. J. Percival, L. J. Small, E. D. Spoecke, and S. B. Rempe, "Polyelectrolyte layer-by-layer deposition on nanoporous supports for ion selective membranes," *RSC Adv.*, vol. 8, no. 57, pp. 32992–32999, 2018, doi: 10.1039/c8ra05580g.

- [102] F. Ben Dhieb, S. H. Tabatabaei, F. Mighri, and A. Ajji, "Comparison of Crosslinking Efficiency in Dip and Roll-Deposited Coatings on Their Oxygen Barrier," *ACS Omega*, vol. 4, no. 14, pp. 15772–15779, 2019, doi: 10.1021/acsomega.9b00950.
- [103] D. Lin, X. Zeng, H. Li, and X. Lai, "Facile fabrication of superhydrophobic and flame-retardant coatings on cotton fabrics via layer-by-layer assembly," *Cellulose*, vol. 25, no. 5, pp. 3135–3149, 2018, doi: 10.1007/s10570-018-1748-9.
- [104] J. Janesch, I. Czabany, C. Hansmann, A. Mautner, T. Rosenau, and W. Gindl-Altmutter, "Transparent layer-by-layer coatings based on biopolymers and CeO₂ to protect wood from UV light," *Prog. Org. Coatings*, vol. 138, no. August 2019, p. 105409, 2020, doi: 10.1016/j.porgcoat.2019.105409.
- [105] Y. Zhang *et al.*, "Eco-friendly flame retardant and electromagnetic interference shielding cotton fabrics with multi-layered coatings," *Chem. Eng. J.*, vol. 372, no. May, pp. 1077–1090, 2019, doi: 10.1016/j.cej.2019.05.012.
- [106] F. Fadhillah, S. M. Javaid Zaidi, Z. Khan, M. Khaled, F. Rahman, and P. Hammond, "Development of multilayer polyelectrolyte thin-film membranes fabricated by spin assisted layer-by-layer assembly," *Journal of Applied Polymer Science*, vol. 126, no. 4, pp. 1468–1474, 2012, doi: 10.1002/app.36879.
- [107] C. J. Lefaux, J. A. Zimmerlin, A. V. Dobrynin, and P. T. Mather, "Polyelectrolyte spin assembly: Influence of ionic strength on the growth of multilayered thin films," *J. Polym. Sci. Part B Polym. Phys.*, vol. 42, no. 19, pp. 3654–3666, 2004, doi: 10.1002/polb.20209.
- [108] F. Oytun and F. Basarir, "Spin-assisted layer-by-layer assembled oppositely charged reduced graphene oxide films," *Mater. Lett.*, vol. 257, p. 126756, 2019, doi: 10.1016/j.matlet.2019.126756.
- [109] W. Yu, J. Koc, J. A. Finlay, J. L. Clarke, A. S. Clare, and A. Rosenhahn, "Layer-by-layer constructed hyaluronic acid/chitosan multilayers as antifouling and fouling-release coatings," *Biointerphases*, vol. 14, no. 5, p. 051002, 2019, doi: 10.1116/1.5110887.
- [110] M. J. Serpe and L. A. Lyon, "Optical and acoustic studies of pH-dependent swelling in microgel thin films," *Chem. Mater.*, vol. 16, no. 22, pp. 4373–4380, 2004, doi: 10.1021/cm048844v.

- [111] V. Vertlib, M. Dietiker, M. Plötze, L. Yezek, R. Spolenak, and A. M. Puzrin, “Fast assembly of bio-inspired nanocomposite films,” *J. Mater. Res.*, vol. 23, no. 4, pp. 1026–1035, 2008, doi: 10.1557/jmr.2008.0147.
- [112] F. Xiang, T. M. Givens, and J. C. Grunlan, “Fast spray deposition of super gas barrier polyelectrolyte multilayer thin films,” *Ind. Eng. Chem. Res.*, vol. 54, no. 19, pp. 5254–5260, 2015, doi: 10.1021/acs.iecr.5b01367.
- [113] Z. Zhou *et al.*, “Layer-by-layer assembly of MXene and carbon nanotubes on electrospun polymer films for flexible energy storage,” *Nanoscale*, vol. 10, no. 13, pp. 6005–6013, 2018, doi: 10.1039/c8nr00313k.
- [114] S. Chang, R. P. Slopek, B. Condon, and J. C. Grunlan, “Surface coating for flame-retardant behavior of cotton fabric using a continuous layer-by-layer process,” *Ind. Eng. Chem. Res.*, vol. 53, no. 10, pp. 3805–3812, 2014, doi: 10.1021/ie403992x.
- [115] K. Fujimoto, S. Fujita, B. Ding, and S. Shiratori, “Fabrication of layer-by-layer self-Assembly films using roll-to-roll process,” *Japanese J. Appl. Physics, Part 2 Lett.*, vol. 44, no. 1–7, pp. 1–4, 2005, doi: 10.1143/JJAP.44.L126.
- [116] F. S. Gittleson, D. J. Kohn, X. Li, and A. D. Taylor, “Improving the assembly speed, quality, and tunability of thin conductive multilayers,” *ACS Nano*, vol. 6, no. 5, pp. 3703–3711, 2012, doi: 10.1021/nn204384f.
- [117] S. Seo, S. Lee, and Y. T. Park, “Note: Automatic layer-by-layer spraying system for functional thin film coatings,” *Rev. Sci. Instrum.*, vol. 87, no. 3, 2016, doi: 10.1063/1.4945043.
- [118] A. J. Mateos, A. A. Cain, and J. C. Grunlan, “Large-scale continuous immersion system for layer-by-layer deposition of flame retardant and conductive nanocoatings on fabric,” *Ind. Eng. Chem. Res.*, vol. 53, no. 15, pp. 6409–6416, 2014, doi: 10.1021/ie500122u.
- [119] F. Carosio and J. Alongi, “Ultra-Fast Layer-by-Layer Approach for Depositing Flame Retardant Coatings on Flexible PU Foams within Seconds,” *ACS Appl. Mater. Interfaces*, vol. 8, no. 10, pp. 6315–6319, 2016, doi: 10.1021/acsami.6b00598.

- [120] S. Miyauchi, H. Imoto, and K. Naka, "Fabrication of polymer-calcite composite thin films by phase transition of vaterite composite particles with octacarboxy-terminated T8-caged silsesquioxane," *Polym. J.*, vol. 48, no. 10, pp. 1019–1027, 2016, doi: 10.1038/pj.2016.69.
- [121] S. Nag, A. Sachan, M. Castro, V. Choudhary, and J. F. Feller, "Spray layer-by-layer assembly of POSS functionalized CNT quantum chemo-resistive sensors with tuneable selectivity and ppm resolution to VOC biomarkers," *Sensors Actuators, B Chem.*, vol. 222, pp. 362–373, 2016, doi: 10.1016/j.snb.2015.08.038.
- [122] B. Song, L. Meng, and Y. Huang, "Preparation and characterization of (POSS/TiO₂)_n multi-coatings based on PBO fiber surface for improvement of UV resistance," *Fibers Polym.*, vol. 14, no. 3, pp. 375–381, 2013, doi: 10.1007/s12221-013-0375-1.
- [123] H. Yang, K. Li, W. Liu, X. Liu, W. Xu, and B. Deng, "Development of structural colored cotton fabric via the layer-by-layer electrostatic self-assembling of SiO₂ nanoparticles," *Cellulose*, vol. 27, no. 7, pp. 4133–4144, 2020, doi: 10.1007/s10570-020-03040-w.
- [124] M. Xiong, Z. Ren, and W. Liu, "Fabrication of UV-resistant and superhydrophobic surface on cotton fabric by functionalized polyethyleneimine/SiO₂ via layer-by-layer assembly and dip-coating," *Cellulose*, vol. 26, no. 16, pp. 8951–8962, 2019, doi: 10.1007/s10570-019-02705-5.
- [125] K. Han, T. Y. Park, K. Yong, and H. J. Cha, "Combinational Biomimicking of Lotus Leaf, Mussel, and Sandcastle Worm for Robust Superhydrophobic Surfaces with Biomedical Multifunctionality: Antithrombotic, Antibiofouling, and Tissue Closure Capabilities," *ACS Appl. Mater. Interfaces*, vol. 11, no. 10, pp. 9777–9785, 2019, doi: 10.1021/acsami.8b21122.
- [126] D. Patra, P. Vangal, A. A. Cain, C. Cho, O. Regev, and J. C. Grunlan, "Inorganic nanoparticle thin film that suppresses flammability of polyurethane with only a single electrostatically-assembled bilayer," *ACS Appl. Mater. Interfaces*, vol. 6, no. 19, pp. 16903–16908, 2014, doi: 10.1021/am504455k.
- [127] K. M. Holder, R. J. Smith, and J. C. Grunlan, "A review of flame retardant nanocoatings prepared using layer-by-layer assembly of polyelectrolytes," *J. Mater. Sci.*, vol. 52, no. 22, pp. 12923–12959, 2017, doi: 10.1007/s10853-017-1390-1.

- [128] K. Srikulkit, C. Iamsamai, and S. T. Dubas, "Development of Flame Retardant Polyphosphoric Acid Coating Based on the Polyelectrolyte Multilayers Technique," *J. Met. Mater. Miner.*, vol. 16, no. 2, pp. 41–45, 2006.
- [129] Y. C. Li, J. Schulz, and J. C. Grunlan, "Polyelectrolyte/nanosilicate thin-film assemblies: Influence of pH on growth, mechanical behavior, and flammability," *ACS Appl. Mater. Interfaces*, vol. 1, no. 10, pp. 2338–2347, 2009, doi: 10.1021/am900484q.
- [130] Y. C. Li *et al.*, "Flame retardant behavior of polyelectrolyte-clay thin film assemblies on cotton fabric," *ACS Nano*, vol. 4, no. 6, pp. 3325–3337, 2010, doi: 10.1021/nn100467e.
- [131] Y. C. Li *et al.*, "Intumescent all-polymer multilayer nanocoating capable of extinguishing flame on fabric," *Advanced Materials*, vol. 23, no. 34, pp. 3926–3931, 2011, doi: 10.1002/adma.201101871.
- [132] A. Laachachi, V. Ball, K. Apaydin, V. Toniazzo, and D. Ruch, "Diffusion of polyphosphates into (poly(allylamine)-montmorillonite) multilayer films: Flame retardant-intumescent films with improved oxygen barrier," *Langmuir*, vol. 27, no. 22, pp. 13879–13887, 2011, doi: 10.1021/la203252q.
- [133] K. Apaydin *et al.*, "Intumescent coating of (polyallylamine-polyphosphates) deposited on polyamide fabrics via layer-by-layer technique," *Polym. Degrad. Stab.*, vol. 106, pp. 158–164, 2014, doi: 10.1016/j.polyimdegradstab.2014.01.006.
- [134] K. Apaydin, A. Laachachi, V. Ball, M. Jimenez, S. Bourbigot, and D. Ruch, "Layer-by-layer deposition of a TiO₂-filled intumescent coating and its effect on the flame retardancy of polyamide and polyester fabrics," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 469, pp. 1–10, 2015, doi: 10.1016/j.colsurfa.2014.12.021.
- [135] M. Haile, M. Leistner, O. Sarwar, C. M. Toler, R. Henderson, and J. C. Grunlan, "A wash-durable polyelectrolyte complex that extinguishes flames on polyester-cotton fabric," *RSC Adv.*, vol. 6, no. 40, pp. 33998–34004, 2016, doi: 10.1039/c6ra03637f.
- [136] G. Laufer, C. Kirkland, A. B. Morgan, and J. C. Grunlan, "Intumescent multilayer nanocoating, made with renewable polyelectrolytes, for flame-retardant cotton," *Biomacromolecules*, vol. 13, no. 9, pp. 2843–2848, 2012, doi: 10.1021/bm300873b.

- [137] Y. Pan and H. Zhao, "A novel blowing agent polyelectrolyte for fabricating intumescent multilayer coating that retards fire on cotton fabric," *J. Appl. Polym. Sci.*, vol. 135, no. 32, pp. 1–8, 2018, doi: 10.1002/app.46583.
- [138] C. K. Kundu, X. Wang, L. Song, and Y. Hu, "Borate cross-linked layer-by-layer assembly of green polyelectrolytes on polyamide 66 fabrics for flame-retardant treatment," *Prog. Org. Coatings*, vol. 121, no. March, pp. 173–181, 2018, doi: 10.1016/j.porgcoat.2018.04.031.
- [139] C. Kumar Kundu *et al.*, "A green approach to constructing multilayered nanocoating for flame retardant treatment of polyamide 66 fabric from chitosan and sodium alginate," *Carbohydr. Polym.*, vol. 166, pp. 131–138, 2017, doi: 10.1016/j.carbpol.2017.02.084.
- [140] X. W. Cheng, J. P. Guan, X. H. Yang, R. C. Tang, and F. Yao, "A bio-resourced phytic acid/chitosan polyelectrolyte complex for the flame retardant treatment of wool fabric," *J. Clean. Prod.*, vol. 223, pp. 342–349, 2019, doi: 10.1016/j.jclepro.2019.03.157.
- [141] M. Jimenez, T. Guin, S. Bellayer, R. Dupretz, S. Bourbigot, and J. C. Grunlan, "Microintumescent mechanism of flame-retardant water-based chitosan-ammonium polyphosphate multilayer nanocoating on cotton fabric," *J. Appl. Polym. Sci.*, vol. 133, no. 32, pp. 1–12, 2016, doi: 10.1002/app.43783.
- [142] F. Fang *et al.*, "Intumescent flame retardant coatings on cotton fabric of chitosan and ammonium polyphosphate via layer-by-layer assembly," *Surf. Coatings Technol.*, vol. 262, pp. 9–14, 2015, doi: 10.1016/j.surfcoat.2014.11.011.
- [143] F. Carosio, J. Alongi, and G. Malucelli, "Layer by Layer ammonium polyphosphate-based coatings for flame retardancy of polyester-cotton blends," *Carbohydr. Polym.*, vol. 88, no. 4, pp. 1460–1469, 2012, doi: 10.1016/j.carbpol.2012.02.049.
- [144] I. Jordanov *et al.*, "Flame retardant polyester fabric from nitrogen-rich low molecular weight additives within intumescent nanocoating," *Polym. Degrad. Stab.*, vol. 170, p. 108998, 2019, doi: 10.1016/j.polymdegradstab.2019.108998.
- [145] F. Carosio and J. Alongi, "Few durable layers suppress cotton combustion due to the joint combination of layer by layer assembly and UV-curing," *RSC Adv.*, vol. 5, no. 87, pp. 71482–71490, 2015, doi: 10.1039/c5ra11856e.

- [146] T. Guin, M. Krecker, A. Milhorn, and J. C. Grunlan, "Maintaining hand and improving fire resistance of cotton fabric through ultrasonication rinsing of multilayer nanocoating," *Cellulose*, vol. 21, no. 4, pp. 3023–3030, 2014, doi: 10.1007/s10570-014-0286-3.
- [147] S. Lazar, B. Eberle, E. Bellevergue, and J. Grunlan, "Amine Salt Thickening of Intumescent Multilayer Flame Retardant Treatment," *Ind. Eng. Chem. Res.*, vol. 59, no. 7, pp. 2689–2695, 2020, doi: 10.1021/acs.iecr.9b06359.
- [148] H. Pan, W. Wang, Y. Pan, L. Song, Y. Hu, and K. M. Liew, "Formation of self-extinguishing flame retardant biobased coating on cotton fabrics via Layer-by-Layer assembly of chitin derivatives," *Carbohydr. Polym.*, vol. 115, pp. 516–524, 2015, doi: 10.1016/j.carbpol.2014.08.084.
- [149] C. K. Kundu, X. Wang, L. Song, and Y. Hu, "Chitosan-based flame retardant coatings for polyamide 66 textiles: One-pot deposition versus layer-by-layer assembly," *Int. J. Biol. Macromol.*, vol. 143, pp. 1–10, 2020, doi: 10.1016/j.ijbiomac.2019.11.220.
- [150] F. Carosio, A. Di Blasio, J. Alongi, and G. Malucelli, "Green DNA-based flame retardant coatings assembled through Layer by Layer," *Polymer (Guildf.)*, vol. 54, no. 19, pp. 5148–5153, 2013, doi: 10.1016/j.polymer.2013.07.029.
- [151] Y. Pan *et al.*, "Effect of genipin crosslinked layer-by-layer self-assembled coating on the thermal stability, flammability and wash durability of cotton fabric," *Carbohydr. Polym.*, vol. 206, no. November 2018, pp. 396–402, 2019, doi: 10.1016/j.carbpol.2018.11.037.
- [152] L. Liu, Y. Pan, Z. Wang, Y. Hou, Z. Gui, and Y. Hu, "Layer-by-Layer Assembly of Hypophosphorous Acid-Modified Chitosan Based Coating for Flame-Retardant Polyester-Cotton Blends," *Ind. Eng. Chem. Res.*, vol. 56, no. 34, pp. 9429–9436, 2017, doi: 10.1021/acs.iecr.7b02303.
- [153] X. Wang, M. Q. Romero, X. Q. Zhang, R. Wang, and D. Y. Wang, "Intumescent multilayer hybrid coating for flame retardant cotton fabrics based on layer-by-layer assembly and sol-gel process," *RSC Adv.*, vol. 5, no. 14, pp. 10647–10655, 2015, doi: 10.1039/c4ra14943b.
- [154] L. Liu, Z. Huang, Y. Pan, X. Wang, L. Song, and Y. Hu, "Finishing of cotton fabrics by multi-layered coatings to improve their flame retardancy and water repellency," *Cellulose*, vol. 25, no. 8, pp. 4791–4803, 2018, doi: 10.1007/s10570-018-1866-4.

- [155] Z. Jiang, C. Wang, S. Fang, P. Ji, H. Wang, and C. Ji, "Durable flame-retardant and antidroplet finishing of polyester fabrics with flexible polysiloxane and phytic acid through layer-by-layer assembly and sol-gel process," *J. Appl. Polym. Sci.*, vol. 135, no. 27, pp. 1–10, 2018, doi: 10.1002/app.46414.
- [156] F. Fang *et al.*, "Environmentally friendly assembly multilayer coating for flame retardant and antimicrobial cotton fabric," *Prog. Org. Coatings*, vol. 90, pp. 258–266, 2016, doi: 10.1016/j.porgcoat.2015.09.025.
- [157] F. Fang *et al.*, "Boron-containing intumescent multilayer nanocoating for extinguishing flame on cotton fabric," *Cellulose*, vol. 23, no. 3, pp. 2161–2172, 2016, doi: 10.1007/s10570-016-0928-8.
- [158] F. Fang *et al.*, "Construction of intumescent flame retardant and antimicrobial coating on cotton fabric via layer-by-layer assembly technology," *Surf. Coatings Technol.*, vol. 276, pp. 726–734, 2015, doi: 10.1016/j.surfcoat.2015.05.023.
- [159] J. C. Yang, W. Liao, S. B. Deng, Z. J. Cao, and Y. Z. Wang, "Flame retardation of cellulose-rich fabrics via a simplified layer-by-layer assembly," *Carbohydr. Polym.*, vol. 151, pp. 434–440, 2016, doi: 10.1016/j.carbpol.2016.05.087.
- [160] T. Zhang, H. Yan, L. Wang, and Z. Fang, "Controlled formation of self-extinguishing intumescent coating on ramie fabric via layer-by-layer assembly," *Ind. Eng. Chem. Res.*, vol. 52, no. 18, pp. 6138–6146, 2013, doi: 10.1021/ie3031554.
- [161] L. Zhao, H. Yan, Z. Fang, J. Wang, and H. Wang, "On the flameproof treatment of ramie fabrics using a spray-assisted layer-by-layer technique," *Polym. Degrad. Stab.*, vol. 121, pp. 11–17, 2015, doi: 10.1016/j.polymdegradstab.2015.08.007.
- [162] F. Carosio, J. Alongi, and G. Malucelli, "Flammability and combustion properties of ammonium polyphosphate-/ poly(acrylic acid)-based layer by layer architectures deposited on cotton, polyester and their blends," *Polym. Degrad. Stab.*, vol. 98, no. 9, pp. 1626–1637, 2013, doi: 10.1016/j.polymdegradstab.2013.06.019.
- [163] F. Carosio, C. Negrell-Guirao, A. Di Blasio, J. Alongi, G. David, and G. Camino, "Tunable thermal and flame response of phosphonated oligoallylamines layer by layer assemblies on cotton," *Carbohydr. Polym.*, vol. 115, pp. 752–759, 2015, doi: 10.1016/j.carbpol.2014.06.066.

- [164] M. Narkhede, S. Thota, R. Mosurkal, W. S. Muller, and J. Kumar, “Layer-by-layer assembly of halogen-free polymeric materials on nylon/cotton blend for flame retardant applications,” *Fire Mater.*, vol. 40, no. 2, pp. 206–218, 2016, doi: 10.1002/fam.
- [165] F. Carosio, F. Cuttica, A. Di Blasio, J. Alongi, and G. Malucelli, “Layer by layer assembly of flame retardant thin films on closed cell PET foams: Efficiency of ammonium polyphosphate versus DNA,” *Polym. Degrad. Stab.*, vol. 113, pp. 189–196, 2015, doi: 10.1016/j.polymdegradstab.2014.09.018.
- [166] S. B. Deng, W. Liao, J. C. Yang, Z. J. Cao, and Y. Z. Wang, “Flame-Retardant and Smoke-Suppressed Silicone Foams with Chitosan-Based Nanocoatings,” *Ind. Eng. Chem. Res.*, vol. 55, no. 27, pp. 7239–7248, 2016, doi: 10.1021/acs.iecr.6b00532.
- [167] F. Carosio, M. Ghanadpour, J. Alongi, and L. Wågberg, “Layer-by-layer-assembled chitosan/phosphorylated cellulose nanofibrils as a bio-based and flame protecting nano-exoskeleton on PU foams,” *Carbohydr. Polym.*, vol. 202, no. July, pp. 479–487, 2018, doi: 10.1016/j.carbpol.2018.09.005.
- [168] H. Xuan, J. Ren, X. Wang, J. Zhang, and L. Ge, “Flame-retardant, non-irritating and self-healing multilayer films with double-network structure,” *Compos. Sci. Technol.*, vol. 145, pp. 15–23, 2017, doi: 10.1016/j.compscitech.2017.03.038.
- [169] O. Köklükaya, F. Carosio, J. C. Grunlan, and L. Wågberg, “Flame-Retardant Paper from Wood Fibers Functionalized via Layer-by-Layer Assembly,” *ACS Appl. Mater. Interfaces*, vol. 7, no. 42, pp. 23750–23759, 2015, doi: 10.1021/acsami.5b08105.
- [170] O. Köklükaya, F. Carosio, and L. Wågberg, “Tailoring flame-retardancy and strength of papers via layer-by-layer treatment of cellulose fibers,” *Cellulose*, vol. 25, no. 4, pp. 2691–2709, 2018, doi: 10.1007/s10570-018-1749-8.
- [171] Y. Pan, L. Liu, and H. Zhao, “Recyclable flame retardant paper made from layer-by-layer assembly of zinc coordinated multi-layered coatings,” *Cellulose*, vol. 25, no. 9, pp. 5309–5321, 2018, doi: 10.1007/s10570-018-1922-0.
- [172] Y. Pan, W. Wang, L. Liu, H. Ge, L. Song, and Y. Hu, “Influences of metal ions crosslinked alginate based coatings on thermal stability and fire resistance of cotton fabrics,” *Carbohydr. Polym.*, vol. 170, pp. 133–139, 2017, doi: 10.1016/j.carbpol.2017.04.065.

- [173] Y. Pan, L. Liu, L. Song, Y. Hu, W. Wang, and H. Zhao, “Durable flame retardant treatment of polyethylene terephthalate (PET) fabric with cross-linked layer-by-layer assembled coating,” *Polym. Degrad. Stab.*, vol. 165, pp. 145–152, 2019, doi: 10.1016/j.polymdegradstab.2019.05.009.
- [174] F. Carosio, G. Fontaine, J. Alongi, and S. Bourbigot, “Starch-Based Layer by Layer Assembly: Efficient and Sustainable Approach to Cotton Fire Protection,” *ACS Appl. Mater. Interfaces*, vol. 7, no. 22, pp. 12158–12167, 2015, doi: 10.1021/acsami.5b02507.
- [175] M. Leistner, A. A. Abu-Odeh, S. C. Rohmer, and J. C. Grunlan, “Water-based chitosan/melamine polyphosphate multilayer nanocoating that extinguishes fire on polyester-cotton fabric,” *Carbohydr. Polym.*, vol. 130, pp. 227–232, 2015, doi: 10.1016/j.carbpol.2015.05.005.
- [176] S. Li, X. Lin, Y. Liu, R. Li, X. Ren, and T. S. Huang, “Phosphorus-nitrogen-silicon-based assembly multilayer coating for the preparation of flame retardant and antimicrobial cotton fabric,” *Cellulose*, vol. 26, no. 6, pp. 4213–4223, 2019, doi: 10.1007/s10570-019-02373-5.
- [177] G. Laufer, C. Kirkland, A. B. Morgan, and J. C. Grunlan, “Exceptionally flame retardant sulfur-based multilayer nanocoating for polyurethane prepared from aqueous polyelectrolyte solutions,” *ACS Macro Lett.*, vol. 2, no. 5, pp. 361–365, 2013, doi: 10.1021/mz400105e.
- [178] Y. Pan *et al.*, “Effect of Fully Biobased Coatings Constructed via Layer-by-Layer Assembly of Chitosan and Lignosulfonate on the Thermal, Flame Retardant, and Mechanical Properties of Flexible Polyurethane Foam,” *ACS Sustain. Chem. Eng.*, vol. 4, no. 3, pp. 1431–1438, 2016, doi: 10.1021/acssuschemeng.5b01423.
- [179] F. Carosio, A. Di Blasio, F. Cuttica, J. Alongi, and G. Malucelli, “Self-assembled hybrid nanoarchitectures deposited on poly(urethane) foams capable of chemically adapting to extreme heat,” *RSC Adv.*, vol. 4, no. 32, pp. 16674–16680, 2014, doi: 10.1039/c4ra01343c.
- [180] F. Carosio, C. Negrell-Guirao, J. Alongi, G. David, and G. Camino, “All-polymer Layer by Layer coating as efficient solution to polyurethane foam flame retardancy,” *Eur. Polym. J.*, vol. 70, pp. 94–103, 2015, doi: 10.1016/j.eurpolymj.2015.07.001.

- [181] J. Chen, S. D. Jiang, Z. Q. Huang, G. Tang, and Y. Hu, "Self-assembly of hydroxyapatite with polyelectrolyte as a green flame retardant for poly(vinyl alcohol)," *J. Fire Sci.*, vol. 35, no. 6, pp. 507–520, 2017, doi: 10.1177/0734904117720476.
- [182] S. D. Jiang, G. Tang, J. Chen, Z. Q. Huang, and Y. Hu, "Biobased polyelectrolyte multilayer-coated hollow mesoporous silica as a green flame retardant for epoxy resin," *J. Hazard. Mater.*, vol. 342, pp. 689–697, 2018, doi: 10.1016/j.jhazmat.2017.09.001.
- [183] H. Yan, N. Li, J. Cheng, P. Song, Z. Fang, and H. Wang, "Fabrication of flame retardant benzoxazine semi-biocomposites reinforced by ramie fabrics with bio-based flame retardant coating," *Polym. Compos.*, vol. 39, pp. E480–E488, 2018, doi: 10.1002/pc.24617.
- [184] N. Li *et al.*, "Flame retarding and reinforcing modification of ramie/polybenzoxazine composites by surface treatment of ramie fabric," *Compos. Sci. Technol.*, vol. 121, pp. 82–88, 2015, doi: 10.1016/j.compscitech.2015.07.013.
- [185] H. Yan, N. Li, Z. Fang, and H. Wang, "Application of poly(diphenolic acid-phenyl phosphate)-based layer by layer nanocoating in flame retardant ramie fabrics," *J. Appl. Polym. Sci.*, vol. 134, no. 20, pp. 1–13, 2017, doi: 10.1002/app.44795.
- [186] X. H. Shi *et al.*, "Layer-by-layer assembled flame-retardant architecture toward high-performance carbon fiber composite," *Chem. Eng. J.*, vol. 353, no. April, pp. 550–558, 2018, doi: 10.1016/j.cej.2018.07.146.
- [187] F. Carosio, G. Laufer, J. Alongi, G. Camino, and J. C. Grunlan, "Layer-by-layer assembly of silica-based flame retardant thin film on PET fabric," *Polym. Degrad. Stab.*, vol. 96, no. 5, pp. 745–750, 2011, doi: 10.1016/j.polymdegradstab.2011.02.019.
- [188] J. Alongi, F. Carosio, A. Frache, and G. Malucelli, "Layer by Layer coatings assembled through dipping, vertical or horizontal spray for cotton flame retardancy," *Carbohydr. Polym.*, vol. 92, no. 1, pp. 114–119, 2013, doi: 10.1016/j.carbpol.2012.08.086.
- [189] F. Carosio, A. Di Blasio, F. Cuttica, J. Alongi, A. Frache, and G. Malucelli, "Flame retardancy of polyester fabrics treated by spray-assisted layer-by-layer silica architectures," *Ind. Eng. Chem. Res.*, vol. 52, no. 28, pp. 9544–9550, 2013, doi: 10.1021/ie4011244.

- [190] F. Carosio, A. Di Blasio, J. Alongi, and G. Malucelli, "Layer by layer nanoarchitectures for the surface protection of polycarbonate," *Eur. Polym. J.*, vol. 49, no. 2, pp. 397–404, 2013, doi: 10.1016/j.eurpolymj.2012.10.032.
- [191] J. Alongi, F. Carosio, and G. Malucelli, "Layer by layer complex architectures based on ammonium polyphosphate, chitosan and silica on polyester-cotton blends: Flammability and combustion behaviour," *Cellulose*, vol. 19, no. 3, pp. 1041–1050, 2012, doi: 10.1007/s10570-012-9682-8.
- [192] H. Yan, L. Zhao, Z. Fang, and H. Wang, "Construction of multilayer coatings for flame retardancy of ramie fabric using layer-by-layer assembly," *Journal of Applied Polymer Science*, vol. 134, no. 48. 2017, doi: 10.1002/app.45556.
- [193] T. Zhang, H. Yan, M. Peng, L. Wang, H. Ding, and Z. Fang, "Construction of flame retardant nanocoating on ramie fabric via layer-by-layer assembly of carbon nanotube and ammonium polyphosphate," *Nanoscale*, vol. 5, no. 7, pp. 3013–3021, 2013, doi: 10.1039/c3nr34020a.
- [194] G. Huang, H. Liang, X. Wang, and J. Gao, "Poly(acrylic acid)/clay thin films assembled by layer-by-layer deposition for improving the flame retardancy properties of cotton," *Ind. Eng. Chem. Res.*, vol. 51, no. 38, pp. 12299–12309, 2012, doi: 10.1021/ie300820k.
- [195] S. Li, X. Lin, Z. Li, and X. Ren, "Hybrid organic-inorganic hydrophobic and intumescent flame-retardant coating for cotton fabrics," *Compos. Commun.*, vol. 14, no. March, pp. 15–20, 2019, doi: 10.1016/j.coco.2019.05.005.
- [196] G. Huang, J. Yang, J. Gao, and X. Wang, "Thin films of intumescent flame retardant-polyacrylamide and exfoliated graphene oxide fabricated via layer-by-layer assembly for improving flame retardant properties of cotton fabric," *Ind. Eng. Chem. Res.*, vol. 51, no. 38, pp. 12355–12366, 2012, doi: 10.1021/ie301911t.
- [197] W. Wang *et al.*, "Synthesis of Phosphorylated Graphene Oxide Based Multilayer Coating: Self-Assembly Method and Application for Improving the Fire Safety of Cotton Fabrics," *Ind. Eng. Chem. Res.*, vol. 56, no. 23, pp. 6664–6670, 2017, doi: 10.1021/acs.iecr.7b01293.
- [198] X. Chen *et al.*, "Flame-retardant, electrically conductive and antimicrobial multifunctional coating on cotton fabric via layer-by-layer assembly technique," *RSC Adv.*, vol. 6, no. 33, pp. 27669–27676, 2016, doi: 10.1039/c5ra26914h.

- [199] X. Ding *et al.*, “Carbon nanotube-filled intumescent multilayer nanocoating on cotton fabric for enhancing flame retardant property,” *Surf. Coatings Technol.*, vol. 305, pp. 184–191, 2016, doi: 10.1016/j.surfcoat.2016.08.035.
- [200] F. Fang *et al.*, “Unique nanobrick wall nanocoating for flame-retardant cotton fabric via layer-by-layer assembly technique,” *Cellulose*, vol. 23, no. 5, pp. 3341–3354, 2016, doi: 10.1007/s10570-016-1013-z.
- [201] F. Carosio, J. Alongi, C. Paravidino, and A. Frache, “Improving the flame retardant efficiency of layer by layer coatings containing deoxyribonucleic acid by post-diffusion of hydrotalcite sanoparticles,” *Materials (Basel)*, vol. 10, no. 7, 2017, doi: 10.3390/ma10070709.
- [202] X. Shi *et al.*, “Bi-phase fire-resistant polyethylenimine/graphene oxide/melanin coatings using layer by layer assembly technique: Smoke suppression and thermal stability of flexible polyurethane foams,” *Polymer (Guildf)*, vol. 170, no. March, pp. 65–75, 2019, doi: 10.1016/j.polymer.2019.03.008.
- [203] A. A. Cain, C. R. Nolen, Y. C. Li, R. Davis, and J. C. Grunlan, “Phosphorous-filled nanobrick wall multilayer thin film eliminates polyurethane melt dripping and reduces heat release associated with fire,” *Polym. Degrad. Stab.*, vol. 98, no. 12, pp. 2645–2652, 2013, doi: 10.1016/j.polymdegradstab.2013.09.028.
- [204] X. Liu *et al.*, “Combination Intumescent and Kaolin-Filled Multilayer Nanocoatings that Reduce Polyurethane Flammability,” *Macromol. Mater. Eng.*, vol. 304, no. 2, pp. 1–7, 2019, doi: 10.1002/mame.201800531.
- [205] O. Köklükaya, F. Carosio, V. L. Durán, and L. Wågberg, “Layer-by-layer modified low density cellulose fiber networks: A sustainable and fireproof alternative to petroleum based foams,” *Carbohydr. Polym.*, vol. 230, no. September 2019, 2020, doi: 10.1016/j.carbpol.2019.115616.
- [206] K. M. Holder, M. E. Huff, M. N. Cosio, and J. C. Grunlan, “Intumescent multilayer thin film deposited on clay-based nanobrick wall to produce self-extinguishing flame retardant polyurethane,” *J. Mater. Sci.*, vol. 50, no. 6, pp. 2451–2458, 2014, doi: 10.1007/s10853-014-8800-4.

- [207] F. Carosio and A. Fina, “Three organic/inorganic nanolayers on flexible foam allow retaining superior flame retardancy performance upon mechanical compression cycles,” *Front. Mater.*, vol. 6, no. February, pp. 1–10, 2019, doi: 10.3389/fmats.2019.00020.
- [208] O. Köklükaya, F. Carosio, and L. Wågberg, “Superior Flame-Resistant Cellulose Nanofibril Aerogels Modified with Hybrid Layer-by-Layer Coatings,” *ACS Appl. Mater. Interfaces*, vol. 9, no. 34, pp. 29082–29092, 2017, doi: 10.1021/acsami.7b08018.
- [209] R. D. Davis, R. H. Harris, and T. Thomas, “Interagency Agreement Report : Exposure and Fire Hazard Assessment of Nanoparticles in Fire Safe Consumer Products NIST Internal Report 7805 Interagency Agreement Report : Exposure and Fire Hazard Assessment of Nanoparticles in Fire Safe Consumer Products,” Gaithersburg, 2011.
- [210] Y. S. Kim, R. Davis, A. A. Cain, and J. C. Grunlan, “Development of layer-by-layer assembled carbon nanofiber-filled coatings to reduce polyurethane foam flammability,” *Polymer (Guildf.)*, vol. 52, no. 13, pp. 2847–2855, 2011, doi: 10.1016/j.polymer.2011.04.023.
- [211] Y. S. Kim and R. Davis, “Multi-walled carbon nanotube layer-by-layer coatings with a trilayer structure to reduce foam flammability,” *Thin Solid Films*, vol. 550, pp. 184–189, 2014, doi: 10.1016/j.tsf.2013.10.167.
- [212] K. M. Holder *et al.*, “Carbon Nanotube Multilayer Nanocoatings Prevent Flame Spread on Flexible Polyurethane Foam,” *Macromol. Mater. Eng.*, vol. 301, no. 6, pp. 665–673, 2016, doi: 10.1002/mame.201500327.
- [213] H. Pan, Y. Pan, W. Wang, L. Song, Y. Hu, and K. M. Liew, “Synergistic effect of layer-by-layer assembled thin films based on clay and carbon nanotubes to reduce the flammability of flexible polyurethane foam,” *Ind. Eng. Chem. Res.*, vol. 53, no. 37, pp. 14315–14321, 2014, doi: 10.1021/ie502215p.
- [214] H. Pan, Y. Lu, L. Song, X. Zhang, and Y. Hu, “Fabrication of binary hybrid-filled layer-by-layer coatings on flexible polyurethane foams and studies on their flame-retardant and thermal properties,” *RSC Adv.*, vol. 6, no. 82, pp. 78286–78295, 2016, doi: 10.1039/c6ra03760g.

- [215] H. Pan, Y. Lu, L. Song, X. Zhang, and Y. Hu, "Construction of layer-by-layer coating based on graphene oxide/ β -FeOOH nanorods and its synergistic effect on improving flame retardancy of flexible polyurethane foam," *Compos. Sci. Technol.*, vol. 129, pp. 116–122, Jun. 2016, doi: 10.1016/j.compscitech.2016.04.018.
- [216] X. Qiu, C. K. Kundu, Z. Li, X. Li, and Z. Zhang, "Layer-by-layer-assembled flame-retardant coatings from polydopamine-induced in situ functionalized and reduced graphene oxide," *J. Mater. Sci.*, vol. 54, no. 21, pp. 13848–13862, 2019, doi: 10.1007/s10853-019-03879-w.
- [217] X. Zhang, Q. Shen, X. Zhang, H. Pan, and Y. Lu, "Graphene oxide-filled multilayer coating to improve flame-retardant and smoke suppression properties of flexible polyurethane foam," *J. Mater. Sci.*, vol. 51, no. 23, pp. 10361–10374, 2016, doi: 10.1007/s10853-016-0247-3.
- [218] F. Carosio, L. Maddalena, J. Gomez, G. Saracco, and A. Fina, "Graphene Oxide Exoskeleton to Produce Self-Extinguishing, Nonignitable, and Flame Resistant Flexible Foams: A Mechanically Tough Alternative to Inorganic Aerogels," *Adv. Mater. Interfaces*, vol. 5, no. 23, pp. 1–9, 2018, doi: 10.1002/admi.201801288.
- [219] H. Pan, B. Yu, W. Wang, Y. Pan, L. Song, and Y. Hu, "Comparative study of layer by layer assembled multilayer films based on graphene oxide and reduced graphene oxide on flexible polyurethane foam: flame retardant and smoke suppression properties," *RSC Adv.*, vol. 6, no. 115, pp. 114304–114312, 2016, doi: 10.1039/c6ra15522g.
- [220] W. Chen *et al.*, "Non-covalently Functionalized Graphene Oxide-Based Coating to Enhance Thermal Stability and Flame Retardancy of PVA Film," *Nano-Micro Lett.*, vol. 10, no. 3, pp. 1–13, 2018, doi: 10.1007/s40820-018-0190-8.
- [221] H. Pan, Y. Pan, L. Song, and Y. Hu, "Construction of β -FeOOH nanorod-filled layer-by-layer coating with effective structure to reduce flammability of flexible polyurethane foam," *Polym. Adv. Technol.*, vol. 28, no. 2, pp. 243–251, Feb. 2017, doi: 10.1002/pat.3880.
- [222] W. Wang *et al.*, "Sandwichlike Coating Consisting of Alternating Montmorillonite and β -FeOOH for Reducing the Fire Hazard of Flexible Polyurethane Foam," *ACS Sustain. Chem. Eng.*, vol. 3, no. 12, pp. 3214–3223, 2015, doi: 10.1021/acssuschemeng.5b00805.

- [223] H. Pan, W. Wang, Y. Pan, L. Song, Y. Hu, and K. M. Liew, "Formation of layer-by-layer assembled titanate nanotubes filled coating on flexible polyurethane foam with improved flame retardant and smoke suppression properties," *ACS Appl. Mater. Interfaces*, vol. 7, no. 1, pp. 101–111, 2015, doi: 10.1021/am507045g.
- [224] M. Haile, S. Fomete, I. D. Lopez, and J. C. Grunlan, "Aluminum hydroxide multilayer assembly capable of extinguishing flame on polyurethane foam," *J. Mater. Sci.*, vol. 51, no. 1, pp. 375–381, 2015, doi: 10.1007/s10853-015-9258-8.
- [225] W. Wang *et al.*, "Synthesis and characterization of MnO₂ nanosheets based multilayer coating and applications as a flame retardant for flexible polyurethane foam," *Compos. Sci. Technol.*, vol. 123, pp. 212–221, 2016, doi: 10.1016/j.compscitech.2015.12.014.
- [226] Y. Pan *et al.*, "Construction of organic–inorganic hybrid nano-coatings containing α -zirconium phosphate with high efficiency for reducing fire hazards of flexible polyurethane foam," *Mater. Chem. Phys.*, vol. 163, pp. 107–115, Aug. 2015, doi: 10.1016/j.matchemphys.2015.07.020.
- [227] H. Pan, Q. Shen, Z. Zhang, B. Yu, and Y. Lu, "MoS₂-filled coating on flexible polyurethane foam via layer-by-layer assembly technique: flame-retardant and smoke suppression properties," *J. Mater. Sci.*, vol. 53, no. 12, pp. 9340–9349, 2018, doi: 10.1007/s10853-018-2199-2.
- [228] B. Lin *et al.*, "MXene/chitosan nanocoating for flexible polyurethane foam towards remarkable fire hazards reductions," *J. Hazard. Mater.*, vol. 381, no. April 2019, 2020, doi: 10.1016/j.jhazmat.2019.120952.
- [229] X. Mu *et al.*, "A single α -cobalt hydroxide/sodium alginate bilayer layer-by-layer assembly for conferring flame retardancy to flexible polyurethane foams," *Mater. Chem. Phys.*, vol. 191, pp. 52–61, 2017, doi: 10.1016/j.matchemphys.2017.01.023.
- [230] X. Qiu, Z. Li, X. Li, L. Yu, and Z. Zhang, "Construction and flame-retardant performance of layer-by-layer assembled hexagonal boron nitride coatings on flexible polyurethane foams," *J. Appl. Polym. Sci.*, vol. 136, no. 29, pp. 1–9, 2019, doi: 10.1002/app.47839.
- [231] A. L. Davesne *et al.*, "Hexagonal Boron Nitride Platelet-Based Nanocoating for Fire Protection," *ACS Appl. Nano Mater.*, vol. 2, no. 9, pp. 5450–5459, 2019, doi: 10.1021/acsanm.9b01055.

- [232] Y. Pan, W. Cai, J. Du, L. Song, Y. Hu, and H. Zhao, “Lanthanum phenylphosphonate–based multilayered coating for reducing flammability and smoke production of flexible polyurethane foam,” *Polym. Adv. Technol.*, vol. 31, no. 6, pp. 1330–1339, 2020, doi: 10.1002/pat.4862.
- [233] L. Liu, W. Wang, and Y. Hu, “Layered double hydroxide-decorated flexible polyurethane foam: Significantly improved toxic effluent elimination,” *RSC Adv.*, vol. 5, no. 118, pp. 97458–97466, 2015, doi: 10.1039/c5ra19414h.
- [234] Y. H. Yang, Y. C. Li, J. Shields, and R. D. Davis, “Layer double hydroxide and sodium montmorillonite multilayer coatings for the flammability reduction of flexible polyurethane foams,” *J. Appl. Polym. Sci.*, vol. 132, no. 14, pp. 1–8, 2015, doi: 10.1002/app.41767.
- [235] Y. C. Li, Y. H. Yang, J. R. Shields, and R. D. Davis, “Layered double hydroxide-based fire resistant coatings for flexible polyurethane foam,” *Polymer (Guildf.)*, vol. 56, pp. 284–292, 2015, doi: 10.1016/j.polymer.2014.11.023.
- [236] H. Pan *et al.*, “Fabrication of flame retardant coating on cotton fabric by alternate assembly of exfoliated layered double hydroxides and alginate,” *RSC Adv.*, vol. 6, no. 113, pp. 111950–111958, 2016, doi: 10.1039/c6ra21804k.
- [237] Y. C. Li, S. Mannen, J. Schulz, and J. C. Grunlan, “Growth and fire protection behavior of POSS-based multilayer thin films,” *J. Mater. Chem.*, vol. 21, no. 9, pp. 3060–3069, 2011, doi: 10.1039/c0jm03752d.
- [238] J. Alongi, A. Di Blasio, F. Carosio, and G. Malucelli, “UV-cured hybrid organic-inorganic Layer by Layer assemblies: Effect on the flame retardancy of polycarbonate films,” *Polym. Degrad. Stab.*, vol. 107, pp. 74–81, 2014, doi: 10.1016/j.polymdegradstab.2014.05.005.
- [239] F. Carosio and J. Alongi, “Influence of layer by layer coatings containing octapropylammonium polyhedral oligomeric silsesquioxane and ammonium polyphosphate on the thermal stability and flammability of acrylic fabrics,” *J. Anal. Appl. Pyrolysis*, vol. 119, pp. 114–123, 2016, doi: 10.1016/j.jaap.2016.03.010.
- [240] Y. Ren, T. Huo, Y. Qin, and X. Liu, “Preparation of flame retardant polyacrylonitrile fabric based on sol-gel and layer-by-layer assembly,” *Materials (Basel)*, vol. 11, no. 4, pp. 1–14, 2018, doi: 10.3390/ma11040483.

- [241] F. Carosio, A. Di Pierro, J. Alongi, A. Fina, and G. Saracco, “Controlling the melt dripping of polyester fabrics by tuning the ionic strength of polyhedral oligomeric silsesquioxane and sodium montmorillonite coatings assembled through Layer by Layer,” *J. Colloid Interface Sci.*, vol. 510, pp. 142–151, 2018, doi: 10.1016/j.jcis.2017.09.059.
- [242] K. Choi, S. Seo, H. Kwon, D. Kim, and Y. T. Park, “Fire protection behavior of layer-by-layer assembled starch–clay multilayers on cotton fabric,” *J. Mater. Sci.*, vol. 53, no. 16, pp. 11433–11443, 2018, doi: 10.1007/s10853-018-2434-x.
- [243] Y. Pan, W. Wang, H. Pan, J. Zhan, and Y. Hu, “Fabrication of montmorillonite and titanate nanotube based coatings: Via layer-by-layer self-assembly method to enhance the thermal stability, flame retardancy and ultraviolet protection of polyethylene terephthalate (PET) fabric,” *RSC Adv.*, vol. 6, no. 59, pp. 53625–53634, 2016, doi: 10.1039/c6ra05213d.
- [244] S. Batool, R. Gill, C. Ma, G. C. S. Reddy, W. Guo, and Y. Hu, “Epoxy-based multilayers for flame resistant flexible polyurethane foam (FPUF),” *J. Appl. Polym. Sci.*, vol. 137, no. 29, pp. 1–10, 2020, doi: 10.1002/app.48890.
- [245] T. Xu, L. Zhang, Y. Zhong, and Z. Mao, “Fire retardancy and durability of poly(N-benzyloxycarbonyl-3,4-dihydroxyphenylalanine)-montmorillonite composite film coated polyimide fabric,” *J. Appl. Polym. Sci.*, vol. 131, no. 1, pp. 1–8, 2014, doi: 10.1002/app.39608.
- [246] Y. S. Kim, R. Harris, and R. Davis, “Innovative approach to rapid growth of highly clay-filled coatings on porous polyurethane foam,” *ACS Macro Lett.*, vol. 1, no. 7, pp. 820–824, 2012, doi: 10.1021/mz300102h.
- [247] Y. C. Li, Y. S. Kim, J. Shields, and R. Davis, “Controlling polyurethane foam flammability and mechanical behaviour by tailoring the composition of clay-based multilayer nanocoatings,” *J. Mater. Chem. A*, vol. 1, no. 41, pp. 12987–12997, 2013, doi: 10.1039/c3ta11936j.
- [248] Y. S. Kim, Y. C. Li, W. M. Pitts, M. Werrel, and R. D. Davis, “Rapid growing clay coatings to reduce the fire threat of furniture,” *ACS Appl. Mater. Interfaces*, vol. 6, no. 3, pp. 2146–2152, 2014, doi: 10.1021/am405259n.

- [249] G. Laufer, C. Kirkland, A. A. Cain, and J. C. Grunlan, “Clay-chitosan nanobrick walls: Completely renewable gas barrier and flame-retardant nanocoatings,” *ACS Applied Materials and Interfaces*, vol. 4, no. 3, pp. 1643–1649, 2012, doi: 10.1021/am2017915.
- [250] W. O. Yah, A. Takahara, and Y. M. Lvov, “Selective modification of halloysite lumen with octadecylphosphonic acid: New inorganic tubular micelle,” *J. Am. Chem. Soc.*, vol. 134, no. 3, pp. 1853–1859, 2012, doi: 10.1021/ja210258y.
- [251] R. J. Smith *et al.*, “Environmentally Benign Halloysite Nanotube Multilayer Assembly Significantly Reduces Polyurethane Flammability,” *Adv. Funct. Mater.*, vol. 28, no. 27, pp. 1–8, 2018, doi: 10.1002/adfm.201703289.
- [252] Y. Pan, L. Liu, W. Cai, Y. Hu, S. Jiang, and H. Zhao, “Effect of layer-by-layer self-assembled sepiolite-based nanocoating on flame retardant and smoke suppressant properties of flexible polyurethane foam,” *Appl. Clay Sci.*, vol. 168, no. November 2018, pp. 230–236, 2019, doi: 10.1016/j.clay.2018.11.014.
- [253] A. A. Cain, M. G. B. Plummer, S. E. Murray, L. Bolling, O. Regev, and J. C. Grunlan, “Iron-containing, high aspect ratio clay as nanoarmor that imparts substantial thermal/flame protection to polyurethane with a single electrostatically-deposited bilayer,” *J. Mater. Chem. A*, vol. 2, no. 41, pp. 17609–17617, 2014, doi: 10.1039/c4ta03541k.
- [254] S. Lazar, F. Carosio, A. L. Davesne, M. Jimenez, S. Bourbigot, and J. Grunlan, “Extreme Heat Shielding of Clay/Chitosan Nanobrick Wall on Flexible Foam,” *ACS Appl. Mater. Interfaces*, vol. 10, no. 37, pp. 31686–31696, 2018, doi: 10.1021/acsami.8b10227.
- [255] T. Guin, M. Kreckler, A. Milhorn, D. A. Hagen, B. Stevens, and J. C. Grunlan, “Exceptional Flame Resistance and Gas Barrier with Thick Multilayer Nanobrick Wall Thin Films,” *Adv. Mater. Interfaces*, vol. 2, no. 11, pp. 1–7, 2015, doi: 10.1002/admi.201500214.
- [256] S. Qin *et al.*, “Super Gas Barrier and Fire Resistance of Nanoplatelet/Nanofibril Multilayer Thin Films,” *Adv. Mater. Interfaces*, vol. 6, no. 2, pp. 1–6, 2019, doi: 10.1002/admi.201801424.

- [257] F. Carosio, J. Kochumalayil, A. Fina, and L. A. Berglund, “Extreme Thermal Shielding Effects in Nanopaper Based on Multilayers of Aligned Clay Nanoplatelets in Cellulose Nanofiber Matrix,” *Adv. Mater. Interfaces*, vol. 3, no. 19, pp. 1–5, 2016, doi: 10.1002/admi.201600551.
- [258] K. Apaydin *et al.*, “Polyallylamine-montmorillonite as super flame retardant coating assemblies by layer-by layer deposition on polyamide,” *Polym. Degrad. Stab.*, vol. 98, no. 2, pp. 627–634, 2013, doi: 10.1016/j.polymdegradstab.2012.11.006.
- [259] K. Apaydin, A. Laachachi, T. Fouquet, M. Jimenez, S. Bourbigot, and D. Ruch, “Mechanistic investigation of a flame retardant coating made by layer-by-layer assembly,” *RSC Adv.*, vol. 4, no. 82, pp. 43326–43334, 2014, doi: 10.1039/c4ra08500k.
- [260] B. Prieur *et al.*, “Phosphorylation of lignin: characterization and investigation of the thermal decomposition,” *RSC Adv.*, vol. 7, no. 27, pp. 16866–16877, 2017, doi: 10.1039/c7ra00295e.
- [261] M. Le Bras, S. Bourbigot, Y. Le Tallec, and J. Laureyns, “Synergy in intumescence - Application to β -cyclodextrin carbonisation agent in intumescent additives for fire retardant polyethylene formulations,” *Polymer Degradation and Stability*, vol. 56, no. 1, pp. 11–21, 1997, doi: 10.1016/S0141-3910(96)00190-5.
- [262] B. ScharTEL, “Phosphorus-based Flame Retardancy Mechanisms—Old Hat or a Starting Point for Future Development?,” *Materials (Basel)*, vol. 3, no. 10, pp. 4710–4745, Sep. 2010, doi: 10.3390/ma3104710.
- [263] M. Lewin and E. D. Weil, “Mechanisms and modes of action in flame retardancy of polymers,” in *Fire Retardant Materials*, A. R. Horrocks and D. Price, Eds. Boca Raton: Woodhead Publishing Limited, 2001, pp. 31–68.
- [264] C. A. Wilkie and A. B. Morgan, *Fire Retardancy of Polymeric Materials*, CRC Press. Boca Raton: CRC Press Taylor and Francis Group, 2010.
- [265] K. M. Gibov, L. N. Shapovalova, and B. A. Zhubanov, “Movement of destruction products through the carbonized layer upon combustion of polymers,” *Fire Mater.*, vol. 10, no. 3–4, pp. 133–135, 1986, doi: 10.1002/fam.810100306.

- [266] A. A. Cain, S. Murray, K. M. Holder, C. R. Nolen, and J. C. Grunlan, “Intumescent nanocoating extinguishes flame on fabric using aqueous polyelectrolyte complex deposited in single step,” *Macromol. Mater. Eng.*, vol. 299, no. 10, pp. 1180–1187, 2014, doi: 10.1002/mame.201400022.
- [267] M. Haile, C. Fincher, S. Fomete, and J. C. Grunlan, “Water-soluble polyelectrolyte complexes that extinguish fire on cotton fabric when deposited as pH-cured nanocoating,” *Polym. Degrad. Stab.*, vol. 114, pp. 60–64, 2015, doi: 10.1016/j.polymdegradstab.2015.01.022.
- [268] X. W. Cheng, R. C. Tang, F. Yao, and X. H. Yang, “Flame retardant coating of wool fabric with phytic acid/polyethyleneimine polyelectrolyte complex,” *Prog. Org. Coatings*, vol. 132, no. March, pp. 336–342, 2019, doi: 10.1016/j.porgcoat.2019.04.018.
- [269] I. S. Zope, S. Foo, D. G. J. Seah, A. T. Akunuri, and A. Dasari, “Development and Evaluation of a Water-Based Flame Retardant Spray Coating for Cotton Fabrics,” *ACS Appl. Mater. Interfaces*, vol. 9, no. 46, pp. 40782–40791, 2017, doi: 10.1021/acsami.7b09863.
- [270] E. M. Elsayed, N. F. Attia, and L. A. Alshehri, “Innovative Flame Retardant and Antibacterial Fabrics Coating Based on Inorganic Nanotubes,” *ChemistrySelect*, vol. 5, no. 10, pp. 2961–2965, 2020, doi: 10.1002/slct.201904182.
- [271] S. Barthwal, S. Barthwal, B. Singh, and N. Bahadur Singh, “Multifunctional and fluorine-free superhydrophobic composite coating based on PDMS modified MWCNTs/ZnO with self-cleaning, oil-water separation, and flame retardant properties,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 597, no. January, p. 124776, 2020, doi: 10.1016/j.colsurfa.2020.124776.
- [272] N. F. Attia and M. Mousa, “Synthesis of smart coating for furniture textile and their flammability and hydrophobic properties,” *Prog. Org. Coatings*, vol. 110, no. April, pp. 204–209, 2017, doi: 10.1016/j.porgcoat.2017.04.035.
- [273] R. Davis, Y. C. Li, M. Gervasio, J. Luu, and Y. S. Kim, “One-pot, bioinspired coatings to reduce the flammability of flexible polyurethane foams,” *ACS Appl. Mater. Interfaces*, vol. 7, no. 11, pp. 6082–6092, 2015, doi: 10.1021/acsami.5b01105.

- [274] F. Carosio, F. Cuttica, L. Medina, and L. A. Berglund, “Clay nanopaper as multifunctional brick and mortar fire protection coating-Wood case study,” *Mater. Des.*, vol. 93, pp. 357–363, 2016, doi: 10.1016/j.matdes.2015.12.140.
- [275] B. Lecouvet, M. Sclavons, S. Bourbigot, and C. Bailly, “Highly loaded nanocomposite films as fire protective coating for polymeric substrates,” *J. Fire Sci.*, vol. 32, no. 2, pp. 145–164, 2014, doi: 10.1177/0734904113500207.
- [276] H. Kim, D. W. Kim, V. Vasagar, H. Ha, S. Nazarenko, and C. J. Ellison, “Polydopamine-Graphene Oxide Flame Retardant Nanocoatings Applied via an Aqueous Liquid Crystalline Scaffold,” *Adv. Funct. Mater.*, vol. 28, no. 39, p. 1803172, Sep. 2018, doi: 10.1002/adfm.201803172.
- [277] A. Walther *et al.*, “Large-area, lightweight and thick biomimetic composites with superior material properties via fast, economic, and green pathways,” *Nano Lett.*, vol. 10, no. 8, pp. 2742–2748, 2010, doi: 10.1021/nl1003224.
- [278] J. George and H. Ishida, “A review on the very high nanofiller-content nanocomposites: Their preparation methods and properties with high aspect ratio fillers,” *Prog. Polym. Sci.*, vol. 86, pp. 1–39, 2018, doi: 10.1016/j.progpolymsci.2018.07.006.
- [279] H. Xie *et al.*, “A highly efficient flame retardant nacre-inspired nanocoating with ultrasensitive fire-warning and self-healing capabilities,” *Chem. Eng. J.*, vol. 369, no. 381, pp. 8–17, 2019, doi: 10.1016/j.cej.2019.03.045.
- [280] H. Xie, X. Lai, Y. Wang, H. Li, and X. Zeng, “A green approach to fabricating nacre-inspired nanocoating for super-efficiently fire-safe polymers via one-step self-assembly,” *J. Hazard. Mater.*, vol. 365, no. 381, pp. 125–136, 2019, doi: 10.1016/j.jhazmat.2018.10.099.
- [281] F. Carosio and J. Alongi, “Flame retardant multilayered coatings on acrylic fabrics prepared by one-step deposition of chitosan/montmorillonite complexes,” *Fibers*, vol. 6, no. 2, pp. 1–11, 2018, doi: 10.3390/fib6020036.
- [282] P. Das, S. Schipmann, J. M. Malho, B. Zhu, U. Klemradt, and A. Walther, “Facile access to large-scale, self-assembled, nacre-inspired, high-performance materials with tunable nanoscale periodicities,” *ACS Appl. Mater. Interfaces*, vol. 5, no. 9, pp. 3738–3747, 2013, doi: 10.1021/am400350q.

- [283] P. Das, H. Thomas, M. Moeller, and A. Walther, “Large-scale, thick, self-assembled, nacre-mimetic brick-walls as fire barrier coatings on textiles,” *Sci. Rep.*, vol. 7, no. November 2016, pp. 1–13, 2017, doi: 10.1038/srep39910.
- [284] F. Ding *et al.*, “Biomimetic nanocoatings with exceptional mechanical, barrier, and flame-retardant properties from large-scale one-step coassembly,” *Sci. Adv.*, vol. 3, no. 7, 2017, doi: 10.1126/sciadv.1701212.
- [285] Y. Pan, L. Liu, X. Wang, L. Song, and Y. Hu, “Hypophosphorous acid cross-linked layer-by-layer assembly of green polyelectrolytes on polyester-cotton blend fabrics for durable flame-retardant treatment,” *Carbohydr. Polym.*, vol. 201, no. March, pp. 1–8, 2018, doi: 10.1016/j.carbpol.2018.08.044.
- [286] J. Liu and C. Xiao, “Fire-retardant multilayer assembled on polyester fabric from water-soluble chitosan, sodium alginate and divalent metal ion,” *Int. J. Biol. Macromol.*, vol. 119, pp. 1083–1089, 2018, doi: 10.1016/j.ijbiomac.2018.08.043.
- [287] W. E. Hennink and C. F. van Nostrum, “Novel crosslinking methods to design hydrogels,” *Adv. Drug Deliv. Rev.*, vol. 64, no. SUPPL., pp. 223–236, 2012, doi: 10.1016/j.addr.2012.09.009.
- [288] N. A. Peppas and A. S. Hoffman, *Hydrogels*, Third Edit. Elsevier, 2013.
- [289] Z. Wang, Y. Cong, and J. Fu, “Stretchable and tough conductive hydrogels for flexible pressure and strain sensors,” *J. Mater. Chem. B*, vol. 8, no. 16, pp. 3437–3459, 2020, doi: 10.1039/c9tb02570g.
- [290] Z. Jiang and G. Dou, “Preparation and Characterization of Chitosan Grafting Hydrogel for Mine-Fire Fighting,” *ACS Omega*, vol. 5, no. 5, pp. 2303–2309, 2020, doi: 10.1021/acsomega.9b03551.
- [291] T. Zhang, Z. Xu, H. Gui, and Q. Guo, “Emulsion-templated, macroporous hydrogels for enhancing water efficiency in fighting fires,” *J. Mater. Chem. A*, vol. 5, no. 21, pp. 10161–10164, 2017, doi: 10.1039/c7ta02319g.
- [292] Y. Li *et al.*, “A novel high-toughness, organic/inorganic double-network fire-retardant gel for coal-seam with high ground temperature,” *Fuel*, vol. 263, no. August 2019, p. 116779, 2020, doi: 10.1016/j.fuel.2019.116779.

- [293] X. Ren *et al.*, “Novel sodium silicate/polymer composite gels for the prevention of spontaneous combustion of coal,” *J. Hazard. Mater.*, vol. 371, no. March, pp. 643–654, 2019, doi: 10.1016/j.jhazmat.2019.03.041.
- [294] Y. Tang and H. Wang, “Development of a novel bentonite–acrylamide superabsorbent hydrogel for extinguishing gangue fire hazard,” *Powder Technol.*, vol. 323, pp. 486–494, 2018, doi: 10.1016/j.powtec.2017.09.051.
- [295] W. Cheng, X. Hu, J. Xie, and Y. Zhao, “An intelligent gel designed to control the spontaneous combustion of coal: Fire prevention and extinguishing properties,” *Fuel*, vol. 210, no. April, pp. 826–835, 2017, doi: 10.1016/j.fuel.2017.09.007.
- [296] A. C. Yu *et al.*, “Scalable manufacturing of biomimetic moldable hydrogels for industrial applications,” *Proc. Natl. Acad. Sci. U. S. A.*, vol. 113, no. 50, pp. 14255–14260, 2016, doi: 10.1073/pnas.1618156113.
- [297] Y. Yang, H. Zhu, Y. T. Tsai, L. Bai, and J. Deng, “Study on the Thermal Stability of Thermosensitive Hydrogel,” *Procedia Eng.*, vol. 135, pp. 501–509, 2016, doi: 10.1016/j.proeng.2016.01.162.
- [298] Y. Yang, J. Deng, D. L. Zhao, and J. Guo, “Mechanism and property of extinguishing temperature-sensitive hydrogels,” *Proc. - 7th Int. Conf. Intell. Comput. Technol. Autom. ICICTA 2014*, pp. 360–364, 2015, doi: 10.1109/ICICTA.2014.94.
- [299] Z. Yu *et al.*, “Preparation and characterisation of fire-resistant PNIPAAm/SA/AgNP thermosensitive network hydrogels and laminated cotton fabric used in firefighter protective clothing,” *Cellulose*, vol. 27, no. 9, pp. 5391–5406, 2020, doi: 10.1007/s10570-020-03146-1.
- [300] W. R. K. Illeperuma, P. Rothemund, Z. Suo, and J. J. Vlassak, “Fire-Resistant Hydrogel-Fabric Laminates: A Simple Concept That May Save Lives,” *ACS Appl. Mater. Interfaces*, vol. 8, no. 3, pp. 2071–2077, 2016, doi: 10.1021/acsami.5b10538.
- [301] J. Wei, G. Wei, Y. Shang, J. Zhou, C. Wu, and Q. Wang, “Dissolution–Crystallization Transition within a Polymer Hydrogel for a Processable Ultratough Electrolyte,” *Adv. Mater.*, vol. 31, no. 30, pp. 1–10, 2019, doi: 10.1002/adma.201900248.

- [302] T. Zhang, Z. Xu, Y. Wu, and Q. Guo, "Assembled Block Copolymer Stabilized High Internal Phase Emulsion Hydrogels for Enhancing Oil Safety," *Ind. Eng. Chem. Res.*, vol. 55, no. 16, pp. 4499–4505, 2016, doi: 10.1021/acs.iecr.6b00039.
- [303] L. Y. Hsiao, L. Jing, K. Li, H. Yang, Y. Li, and P. Y. Chen, "Carbon nanotube-integrated conductive hydrogels as multifunctional robotic skin," *Carbon N. Y.*, vol. 161, pp. 784–793, 2020, doi: 10.1016/j.carbon.2020.01.109.
- [304] X. F. Cui *et al.*, "Water-retaining, tough and self-healing hydrogels and their uses as fire-resistant materials," *Polym. Chem.*, vol. 10, no. 37, pp. 5151–5158, 2019, doi: 10.1039/c9py01015g.
- [305] B. N. Mallick, P. K. Rana, and P. K. Sahoo, "Preparation of Starch-Based Bionanocomposite Hydrogel with Mica for Fire Retardancy," *Adv. Polym. Technol.*, vol. 34, no. 4, p. 21520, Dec. 2015, doi: 10.1002/adv.21520.
- [306] L. Geoffroy *et al.*, "3D printed sandwich materials filled with hydrogels for extremely low heat release rate," *Polym. Degrad. Stab.*, vol. 179, p. 109269, 2020, doi: 10.1016/j.polymdegradstab.2020.109269.
- [307] C. Chen *et al.*, "Compressive, ultralight and fire-resistant lignin-modified graphene aerogels as recyclable absorbents for oil and organic solvents," *Chem. Eng. J.*, vol. 350, no. January, pp. 173–180, 2018, doi: 10.1016/j.cej.2018.05.189.
- [308] L. Zuo *et al.*, "Graphene/montmorillonite hybrid synergistically reinforced polyimide composite aerogels with enhanced flame-retardant performance," *Compos. Sci. Technol.*, vol. 139, pp. 57–63, 2017, doi: 10.1016/j.compscitech.2016.12.008.
- [309] Y. Wang *et al.*, "Multifunctional polyimide aerogel textile inspired by polar bear hair for thermoregulation in extreme environments," *Chem. Eng. J.*, vol. 390, no. January, p. 124623, 2020, doi: 10.1016/j.cej.2020.124623.
- [310] Z. Qian *et al.*, "Fire-resistant, ultralight, superelastic and thermally insulated polybenzazole aerogels," *J. Mater. Chem. A*, vol. 6, no. 42, pp. 20769–20777, 2018, doi: 10.1039/C8TA07204C.
- [311] M. Kaya and A. Tabak, "Recycling of an Agricultural Bio-waste as a Novel Cellulose Aerogel: A Green Chemistry Study," *J. Polym. Environ.*, vol. 28, no. 1, pp. 323–330, 2020, doi: 10.1007/s10924-019-01609-6.

- [312] X. Luo, J. Shen, Y. Ma, L. Liu, R. Meng, and J. Yao, “Robust, sustainable cellulose composite aerogels with outstanding flame retardancy and thermal insulation,” *Carbohydr. Polym.*, vol. 230, no. November 2019, p. 115623, 2020, doi: 10.1016/j.carbpol.2019.115623.
- [313] Y. Han, X. Zhang, X. Wu, and C. Lu, “Flame Retardant, Heat Insulating Cellulose Aerogels from Waste Cotton Fabrics by in Situ Formation of Magnesium Hydroxide Nanoparticles in Cellulose Gel Nanostructures,” *ACS Sustain. Chem. Eng.*, vol. 3, no. 8, pp. 1853–1859, 2015, doi: 10.1021/acssuschemeng.5b00438.
- [314] M. Kaya, “Super absorbent, light, and highly flame retardant cellulose-based aerogel crosslinked with citric acid,” *J. Appl. Polym. Sci.*, vol. 134, no. 38, p. 45315, Oct. 2017, doi: 10.1002/app.45315.
- [315] X. Zhou *et al.*, “Excellent flame retardant and thermal insulated palygorskite/wood fiber composite aerogels with improved mechanical properties,” *Appl. Clay Sci.*, vol. 184, no. August 2019, p. 105402, 2020, doi: 10.1016/j.clay.2019.105402.
- [316] M. Farooq, M. H. Sipponen, A. Seppälä, and M. Österberg, “Eco-friendly Flame-Retardant Cellulose Nanofibril Aerogels by Incorporating Sodium Bicarbonate,” *ACS Appl. Mater. Interfaces*, vol. 10, no. 32, pp. 27407–27415, 2018, doi: 10.1021/acami.8b04376.
- [317] D. Wang *et al.*, “Biomimetic structural cellulose nanofiber aerogels with exceptional mechanical, flame-retardant and thermal-insulating properties,” *Chem. Eng. J.*, vol. 389, no. February, p. 124449, 2020, doi: 10.1016/j.cej.2020.124449.
- [318] B. Wicklein *et al.*, “Thermally insulating and fire-retardant lightweight anisotropic foams based on nanocellulose and graphene oxide,” *Nat. Nanotechnol.*, vol. 10, no. 3, pp. 277–283, 2015, doi: 10.1038/nnano.2014.248.
- [319] L. Wang and M. Sánchez-Soto, “Green bio-based aerogels prepared from recycled cellulose fiber suspensions,” *RSC Adv.*, vol. 5, no. 40, pp. 31384–31391, 2015, doi: 10.1039/c5ra02981c.
- [320] L. Guo, Z. Chen, S. Lyu, F. Fu, and S. Wang, “Highly flexible cross-linked cellulose nanofibril sponge-like aerogels with improved mechanical property and enhanced flame retardancy,” *Carbohydr. Polym.*, vol. 179, no. September 2017, pp. 333–340, 2018, doi: 10.1016/j.carbpol.2017.09.084.

- [321] Z. Zhou, Y. Yang, Y. Han, Q. Guo, X. Zhang, and C. Lu, "In situ doping enables the multifunctionalization of templately synthesized polyaniline@cellulose nanocomposites," *Carbohydr. Polym.*, vol. 177, no. August, pp. 241–248, 2017, doi: 10.1016/j.carbpol.2017.08.136.
- [322] W. Guo, X. Wang, P. Zhang, J. Liu, L. Song, and Y. Hu, "Nano-fibrillated cellulose-hydroxyapatite based composite foams with excellent fire resistance," *Carbohydr. Polym.*, vol. 195, no. November 2017, pp. 71–78, 2018, doi: 10.1016/j.carbpol.2018.04.063.
- [323] L. Wang, M. Sánchez-Soto, J. Fan, Z. Xia, and Y. Liu, "Boron/nitrogen flame retardant additives cross-linked cellulose nanofibril/montmorillonite aerogels toward super-low flammability and improved mechanical properties," *Polym. Adv. Technol.*, vol. 30, no. 7, pp. 1807–1817, Jul. 2019, doi: 10.1002/pat.4613.
- [324] W. Guo, J. Liu, P. Zhang, L. Song, X. Wang, and Y. Hu, "Multi-functional hydroxyapatite/polyvinyl alcohol composite aerogels with self-cleaning, superior fire resistance and low thermal conductivity," *Compos. Sci. Technol.*, vol. 158, pp. 128–136, 2018, doi: 10.1016/j.compscitech.2018.01.020.
- [325] H. B. Chen, X. L. Li, M. J. Chen, Y. R. He, and H. B. Zhao, "Self-cross-linked melamine-formaldehyde-pectin aerogel with excellent water resistance and flame retardancy," *Carbohydr. Polym.*, vol. 206, no. October 2018, pp. 609–615, 2019, doi: 10.1016/j.carbpol.2018.11.041.
- [326] X. L. Li, Y. R. He, Z. M. Qin, M. J. Chen, and H. B. Chen, "Facile fabrication, mechanical property and flame retardancy of aerogel composites based on alginate and melamine-formaldehyde," *Polymer (Guildf.)*, vol. 181, no. June, p. 121783, 2019, doi: 10.1016/j.polymer.2019.121783.
- [327] K. Shang, J. C. Yang, Z. J. Cao, W. Liao, Y. Z. Wang, and D. A. Schiraldi, "Novel Polymer Aerogel toward High Dimensional Stability, Mechanical Property, and Fire Safety," *ACS Appl. Mater. Interfaces*, vol. 9, no. 27, pp. 22985–22993, 2017, doi: 10.1021/acsami.7b06096.
- [328] Y. Huang *et al.*, "Flame-retardant polyvinyl alcohol/cellulose nanofibers hybrid carbon aerogel by freeze drying with ultra-low phosphorus," *Appl. Surf. Sci.*, vol. 497, no. August, p. 143775, 2019, doi: 10.1016/j.apsusc.2019.143775.

- [329] A. H. Kang *et al.*, “Rejuvenated fly ash in poly(vinyl alcohol)-based composite aerogels with high fire safety and smoke suppression,” *Chem. Eng. J.*, vol. 327, pp. 992–999, 2017, doi: 10.1016/j.cej.2017.06.158.
- [330] H. B. Chen, Y. Z. Wang, and D. A. Schiraldi, “Preparation and flammability of poly(vinyl alcohol) composite aerogels,” *ACS Appl. Mater. Interfaces*, vol. 6, no. 9, pp. 6790–6796, 2014, doi: 10.1021/am500583x.
- [331] Y. Luo *et al.*, “Synergistic effect of ammonium polyphosphate and α -zirconium phosphate in flame-retardant poly(vinyl alcohol) aerogels,” *Polym. Degrad. Stab.*, vol. 170, p. 109019, Dec. 2019, doi: 10.1016/j.polymdegradstab.2019.109019.
- [332] X. Sheng, S. Li, Y. Zhao, D. Zhai, L. Zhang, and X. Lu, “Synergistic effects of two-dimensional mxene and ammonium polyphosphate on enhancing the fire safety of polyvinyl alcohol composite aerogels,” *Polymers (Basel)*, vol. 11, no. 12, pp. 1–17, 2019, doi: 10.3390/polym11121964.
- [333] Q. Zhang, X. Wang, X. Tao, Z. Li, X. Li, and Z. Zhang, “Polyvinyl alcohol composite aerogel with remarkable flame retardancy, chemical durability and self-cleaning property,” *Compos. Commun.*, vol. 15, no. May, pp. 96–102, 2019, doi: 10.1016/j.coco.2019.07.003.
- [334] L. Medina, F. Carosio, and L. A. Berglund, “Recyclable nanocomposite foams of Poly(vinyl alcohol), clay and cellulose nanofibrils – Mechanical properties and flame retardancy,” *Compos. Sci. Technol.*, vol. 182, no. May, p. 107762, 2019, doi: 10.1016/j.compscitech.2019.107762.
- [335] Y. T. Wang *et al.*, “Green Approach to Improving the Strength and Flame Retardancy of Poly(vinyl alcohol)/Clay Aerogels: Incorporating Biobased Gelatin,” *ACS Appl. Mater. Interfaces*, vol. 9, no. 48, pp. 42258–42265, 2017, doi: 10.1021/acsami.7b14958.
- [336] L. Wang, M. Sánchez-Soto, and M. L. Maspocho, “Polymer/clay aerogel composites with flame retardant agents: Mechanical, thermal and fire behavior,” *Mater. Des.*, vol. 52, pp. 609–614, 2013, doi: 10.1016/j.matdes.2013.05.096.
- [337] K. Shang *et al.*, “Robust and fire retardant borate-crosslinked poly (vinyl alcohol)/montmorillonite aerogel via melt-crosslink,” *Polymer (Guildf)*, vol. 131, pp. 111–119, 2017, doi: 10.1016/j.polymer.2017.07.022.

- [338] A. Liu, L. Medina, and L. A. Berglund, “High-Strength Nanocomposite Aerogels of Ternary Composition: Poly(vinyl alcohol), Clay, and Cellulose Nanofibrils,” *ACS Appl. Mater. Interfaces*, vol. 9, no. 7, pp. 6453–6461, 2017, doi: 10.1021/acsami.6b15561.
- [339] H. B. Chen *et al.*, “Fabrication and properties of irradiation-cross-linked poly(vinyl alcohol)/clay aerogel composites,” *ACS Appl. Mater. Interfaces*, vol. 6, no. 18, pp. 16227–16236, 2014, doi: 10.1021/am504418w.
- [340] H. B. Zhao, M. Chen, and H. B. Chen, “Thermally Insulating and Flame-Retardant Polyaniline/Pectin Aerogels,” *ACS Sustain. Chem. Eng.*, vol. 5, no. 8, pp. 7012–7019, 2017, doi: 10.1021/acssuschemeng.7b01247.
- [341] D. D. Ye *et al.*, “Ultrahigh-Temperature Insulating and Fire-Resistant Aerogels from Cationic Amylopectin and Clay via a Facile Route,” *ACS Sustain. Chem. Eng.*, vol. 7, no. 13, pp. 11582–11592, 2019, doi: 10.1021/acssuschemeng.9b01487.
- [342] W. Yang *et al.*, “Pectin-assisted dispersion of exfoliated boron nitride nanosheets for assembled bio-composite aerogels,” *Compos. Part A Appl. Sci. Manuf.*, vol. 119, no. December 2018, pp. 196–205, 2019, doi: 10.1016/j.compositesa.2019.02.003.
- [343] J. Zhu *et al.*, “Lightweight, High-Strength, and Anisotropic Structure Composite Aerogel Based on Hydroxyapatite Nanocrystal and Chitosan with Thermal Insulation and Flame Retardant Properties,” *ACS Sustain. Chem. Eng.*, vol. 8, no. 1, pp. 71–83, 2020, doi: 10.1021/acssuschemeng.9b03953.
- [344] L. Wang, D. A. Schiraldi, and M. Sánchez-Soto, “Foamlike xanthan gum/clay aerogel composites and tailoring properties by blending with agar,” *Ind. Eng. Chem. Res.*, vol. 53, no. 18, pp. 7680–7687, 2014, doi: 10.1021/ie500490n.
- [345] L. Wang, M. Sánchez-Soto, and T. Abt, “Properties of bio-based gum Arabic/clay aerogels,” *Ind. Crops Prod.*, vol. 91, pp. 15–21, 2016, doi: 10.1016/j.indcrop.2016.05.001.
- [346] H. Jin *et al.*, “Ultralight and Hydrophobic Palygorskite-based Aerogels with Prominent Thermal Insulation and Flame Retardancy,” *ACS Appl. Mater. Interfaces*, vol. 12, no. 10, pp. 11815–11824, 2020, doi: 10.1021/acsami.9b20923.

- [347] K. Shang, W. Liao, J. Wang, Y. T. Wang, Y. Z. Wang, and D. A. Schiraldi, “Nonflammable Alginate Nanocomposite Aerogels Prepared by a Simple Freeze-Drying and Post-Cross-Linking Method,” *ACS Appl. Mater. Interfaces*, vol. 8, no. 1, pp. 643–650, 2016, doi: 10.1021/acsami.5b09768.
- [348] H. B. Chen, Y. Y. Ao, D. Liu, H. T. Song, and P. Shen, “Novel Neutron Shielding Alginate Based Aerogel with Extremely Low Flammability,” *Ind. Eng. Chem. Res.*, vol. 56, no. 30, pp. 8563–8567, 2017, doi: 10.1021/acs.iecr.7b01999.
- [349] X. L. Li, M. J. Chen, and H. B. Chen, “Facile fabrication of mechanically-strong and flame retardant alginate/clay aerogels,” *Compos. Part B Eng.*, vol. 164, no. November 2018, pp. 18–25, 2019, doi: 10.1016/j.compositesb.2018.11.055.
- [350] Q. Wang *et al.*, “Facile construction of cellulose/montmorillonite nanocomposite biobased plastics with flame retardant and gas barrier properties,” *Cellulose*, vol. 22, no. 6, pp. 3799–3810, 2015, doi: 10.1007/s10570-015-0758-0.
- [351] X. Zhang, B. Wu, S. Sun, and P. Wu, “Hybrid Materials from Ultrahigh-Inorganic-Content Mineral Plastic Hydrogels: Arbitrarily Shapeable, Strong, and Tough,” *Adv. Funct. Mater.*, vol. 30, no. 19, p. 1910425, May 2020, doi: 10.1002/adfm.201910425.
- [352] O. Gady, M. Poirson, T. Vincent, R. Sonnier, and E. Guibal, “Elaboration of light composite materials based on alginate and algal biomass for flame retardancy: preliminary tests,” *J. Mater. Sci.*, vol. 51, no. 22, pp. 10035–10047, 2016, doi: 10.1007/s10853-016-0230-z.
- [353] M. Försth, S. Zhao, and A. Roos, “Spectrally selective and adaptive surfaces for protection against radiative heating: ITO and VO₂,” *Fire Mater.*, vol. 38, pp. 111–124, 2014, doi: 10.1002/fam.2167.
- [354] J. F. Sacadura, “Radiative heat transfer in fire safety science,” *J. Quant. Spectrosc. Radiat. Transf.*, vol. 93, no. 1-3 SPEC. ISS., pp. 5–24, 2005, doi: 10.1016/j.jqsrt.2004.08.011.
- [355] J. de Ris, “Fire radiation-A review,” *Symp. Combust.*, vol. 17, no. 1, pp. 1003–1016, 1979, doi: 10.1016/S0082-0784(79)80097-1.
- [356] J. De Ris, “A Scientific Approach To Flame Radiation And Material Flammability,” *Fire Saf. Sci.*, vol. 2, pp. 29–46, 1989, doi: 10.3801/iafss.fss.2-29.

- [357] A. Miller, “Fundamental Optical Properties of Solids,” in *Handbook of optics, volume I*, 2nd ed., M. Bass, E. W. Van Stryland, D. R. Williams, and W. L. Wolfe, Eds. New York: McGraw-Hill, Inc, 1995, pp. 1–33.
- [358] M. J. Riedl, *Optical Design Fundamentals for Infrared Systems, Second Edition*. Washington D.C.: SPIE Press, 2001.
- [359] M. F. Modest, “Fundamentals of Thermal Radiation,” in *Radiative Heat Transfer*, 3rd ed., Oxford: Elsevier, 2013, pp. 1–30.
- [360] F. Kreith *et al.*, “Heat and mass transfer,” in *Mechanical Engineering Handbook*, 1st ed., F. Kreith, Ed. Boca Raton: CRC Press LLC, 1999.
- [361] P. Patel, T. R. Hull, A. A. Stec, and R. E. Lyon, “Influence of physical properties on polymer flammability in the cone calorimeter,” *Polym. Adv. Technol.*, vol. 22, no. 7, pp. 1100–1107, 2011, doi: 10.1002/pat.1943.
- [362] N. Roenner, H. Yuan, R. H. Krämer, and G. Rein, “Computational study of how inert additives affect the flammability of a polymer,” *Fire Saf. J.*, vol. 106, no. December 2018, pp. 189–196, 2019, doi: 10.1016/j.firesaf.2019.04.013.
- [363] I. Vermesi, N. Roenner, P. Pironi, R. M. Hadden, and G. Rein, “Pyrolysis and ignition of a polymer by transient irradiation,” *Combust. Flame*, vol. 163, pp. 31–41, 2016, doi: 10.1016/j.combustflame.2015.08.006.
- [364] T. Nyazika, “Conceptualization of a fire barrier: fundamentals and experimental approach,” Université de Lille, 2019.
- [365] M. Boccas, T. Vucina, C. Araya, E. Vera, and C. Ahhee, “Coating the 8-m Gemini telescopes with protected silver,” *Opt. Fabr. Metrol. Mater. Adv. Telesc.*, vol. 5494, no. May, p. 239, 2004, doi: 10.1117/12.548809.
- [366] N. L. Thomas, J. D. Wolfe, and J. C. Farmer, “Protected silver coating for astronomical mirrors,” in *Advanced Technology Optical/IR Telescopes VI*, Aug. 1998, vol. 3352, no. May, pp. 580–586, doi: 10.1117/12.319243.
- [367] C. Xu *et al.*, “An optically transparent sandwich structure for radar-infrared bi-stealth,” *Infrared Phys. Technol.*, vol. 105, no. September 2019, p. 103108, 2020, doi: 10.1016/j.infrared.2019.103108.

- [368] L. Peng, D. Liu, H. Cheng, S. Zhou, and M. Zu, “A Multilayer Film Based Selective Thermal Emitter for Infrared Stealth Technology,” *Adv. Opt. Mater.*, vol. 6, no. 23, pp. 1–8, 2018, doi: 10.1002/adom.201801006.
- [369] Z. Mao, X. Yu, L. Zhang, Y. Zhong, and H. Xu, “Novel infrared stealth property of cotton fabrics coated with nano ZnO: (Al, La) particles,” *Vacuum*, vol. 104, pp. 111–115, 2014, doi: 10.1016/j.vacuum.2014.01.011.
- [370] G. K. Dalapati *et al.*, “Transparent heat regulating (THR) materials and coatings for energy saving window applications: Impact of materials design, micro-structural, and interface quality on the THR performance,” *Prog. Mater. Sci.*, vol. 95, pp. 42–131, 2018, doi: 10.1016/j.pmatsci.2018.02.007.
- [371] M. Ohring, “Mechanical Properties of Thin Films,” in *Materials Science of Thin Films*, 2nd ed., A. Press, Ed. San Diego: Elsevier, 2002, pp. 711–781.
- [372] P. H. Berdahl, “Pigments which Reflect Infrared Radiation from Fire,” 5,811,180, 1998.
- [373] P. Berdahl, “Pigments to reflect the infrared radiation from fire,” *J. Heat Transfer*, vol. 117, no. 2, pp. 355–358, 1995, doi: 10.1115/1.2822529.
- [374] P. Berdahl, “Building energy efficiency and fire safety aspects of reflective coatings,” *Energy Build.*, vol. 22, no. 3, pp. 187–191, 1995, doi: 10.1016/0378-7788(95)00921-J.
- [375] J. Zhao *et al.*, “The high-temperature resistance properties of polysiloxane/Al coatings with low infrared emissivity,” *Coatings*, vol. 8, no. 4, 2018, doi: 10.3390/coatings8040125.
- [376] L. Qi *et al.*, “Effects of low-melting glass powder on the thermal stabilities of low infrared emissivity Al/polysiloxane coatings,” *Prog. Org. Coatings*, vol. 142, no. January, p. 105579, 2020, doi: 10.1016/j.porgcoat.2020.105579.
- [377] R. Sonnier, L. Ferry, B. Gallard, A. Boudenne, and F. Lavaud, “Controlled emissivity coatings to delay ignition of polyethylene,” *Materials (Basel)*, vol. 8, no. 10, pp. 6935–6949, 2015, doi: 10.3390/ma8105349.
- [378] B. Schartel, U. Beck, H. Bahr, A. Hertwig, U. Knoll, and M. Weise, “Sub-micrometre coatings as an infrared mirror: A new route to flame retardancy,” *Fire Mater.*, vol. 36, pp. 671–677, 2012, doi: 10.1002/fam.1122.

- [379] R. Ochoterena and M. Försth, “The effect of thermochromic coatings of VO₂ on the fire performance of windows,” *Fire Mater.*, vol. 42, no. 7, pp. 873–876, Nov. 2018, doi: 10.1002/fam.2630.
- [380] A.-L. Davesne *et al.*, “Low-Emissivity Metal/Dielectric Coatings as Radiative Barriers for the Fire Protection of Raw and Formulated Polymers,” *ACS Appl. Polym. Mater.*, 2020, doi: 10.1021/acsapm.0c00399.