

# 14 Conformal Flame Retardant Coating Systems

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## 14.1 MEETING THE FLAMMABILITY CHALLENGE AT THE INTERFACE

Flame retardant (FR) surface treatments have been a target of scientific and industrial focus for many decades.<sup>1</sup> The development of coating technologies was borne out of a combination of necessity and convenience. Necessity due to the fact that natural fibers such as cotton cannot be coextruded with a flame retardant FR molecule in a manner analogous to synthetic polyester or polyamide fabrics. Convenience in the sense that the processing equipment to finish textiles has been refined for centuries to apply dyes or other finishes to fabrics. Flame-retardant finishes are a natural extension of these conditions, and flame-retardant treatments for textiles have been an active research topic ever since. Please see Chapter 27 of this book for more information on textile flammability and fire protection.

Inadvertently, the development of flame retardant textile finishes stumbled upon a critical advantage in the fight against fire and flammability: surface area. In the decades since the first flame retardant textile finishes appeared, researchers have become keenly aware of the importance of surface area and localization of flame retardant chemistries to impart fire protection to materials. Combustion naturally begins at the exterior of a sample, meaning that surface treatments will yield materials with a higher ratio of FR:substrate in the early stages of combustion. This is critical to mitigate the hazards of material flammability. Additionally, the use of a surface treatment mitigates the degradation of mechanical properties brought on by incorporation of bulk additives.<sup>2</sup> When a surface treatment can be easily removed at the end of a product's life cycle, the underlying material can be more easily recycled. Increasing the potential for material recyclability and circularity makes surface treatments a core research focus. For these reasons, surface treatments for fire protection have become a major area of academic and industrial investment in recent years.<sup>3</sup>

In this chapter, we will outline some of the key substrates that benefit most from surface treatments for flammability reduction and introduce the major techniques to apply such treatments. Particular attention will be paid to the material and process sustainability of the outlined techniques. We note that many techniques that could broadly be classified as “covalent surface modification” inasmuch as they yield a mostly unaltered (at both macro- and microscopic length scales) surface could be considered conformal treatments. Many of those chemistries are covered more thoroughly in other chapters and, as such, will only be minimally addressed in this chapter.

### 14.1.1 COMMON SUBSTRATES FOR FLAME-RETARDANT SURFACE TREATMENTS

#### 14.1.1.1 Textiles

As previously noted, textiles were some of the first substrates where coating technologies for flammability reduction became commonplace.<sup>1</sup> Textiles remain a critical substrate to protect due to the widespread prevalence of severe injuries and deaths related to clothing burns, especially from synthetic fibers such as polyester and polyamide that are prone to melting.<sup>4</sup> Naturally derived cotton and synthetic fibers such as polyesters (most often polyethylene terephthalate, PET) or polyamides (most often polyamide-6,6 or simply abbreviated as PA), and their blends with cotton, are the subject of most textile flammability research. The degradation pathways of cotton, which is cellulosic, and synthetic fibers are markedly different and require different chemistries in order to reduce their flammability.

Cotton's thermal decomposition occurs in a two-stage process, beginning with a dehydroxylation and partial charring.<sup>5</sup> The initial degradation step preserves the structure of the cotton, and this is followed by a diffusion-controlled oxidation of the charred material. Cotton's relatively high char yield and low tendency to produce flammable volatiles

during its decomposition are the cause of its relatively low heat release. The tendency of cotton to form carbonaceous material is leveraged by intumescent treatments, which are designed to promote cross-linking and density of the charred area. The cross-linked char yields a material that is more resistant to the secondary oxidation step.<sup>6</sup> As a result, many FR treatments for cotton and other natural fibers are phosphorus-based, leveraging cotton's tendency to char to their advantage.

In contrast, synthetic fibers do not tend to form char as they decompose. Rather, they typically depolymerize into lower molecular weight oligomers during pyrolysis.<sup>7,8</sup> Instead of preserving the fibrous structure like cotton does, synthetic fibers are instead prone to melt dripping.<sup>9</sup> This dripping promotes flame spread but moreover poses a challenge in arresting flame spread since there is no easy scaffold for maintaining structure and promoting char formation. In addition to the depolymerization and melt behavior, synthetic fibers based upon aliphatic carbon chemistry (polyolefins, aliphatic nylons) have a higher total heat release (THR) and peak heat release rate (pkHRR) than cotton.<sup>10</sup> Blends of cotton and synthetic fibers such as polyester-cotton (PECO) or nylon-cotton (NYCO) are commonplace to take advantage of the robustness of synthetic fibers and the breathability and comfort of cotton. Blends pose a particular flammability challenge because the charring of the cotton in the blend provides a scaffold for faster flame spread as the synthetic component degrades, yielding extremely flammable fabrics.<sup>11</sup>

#### 14.1.1.2 Wood

Home structure fires are responsible for approximately three quarters of fire deaths in the United States.<sup>12</sup> Wood is a common building component in home construction and as such is a critical substrate for fire protection. There has also been an added emphasis on the flammability of outdoor wood structures (e.g., fences) owing to their tendency to propagate wildfires.<sup>13</sup> Wood has a high fraction of cellulose and as such exhibits many of the same degradation properties as cotton. The early stages of wood degradation lead to the removal of aliphatic materials, which are lost as CO<sub>2</sub> or become aromatic char.<sup>14</sup> Despite this mass loss, the porosity of wood does not increase appreciably during the early stages of thermal degradation (up to ~250°C) but does increase notably at higher temperatures when aromatic carbon begins to degrade. Please see Chapter 26 of this book for more information on wood flammability and fire protection approaches.

Wood has slow diffusion kinetics owing to its very complex surface. These slow transport properties mean that, unlike in the cases of textiles or foam, coatings are unlikely to permeate the entirety of a treated piece of wood.<sup>15</sup> Much like cotton, char promotion via phosphorus-based FRs have been demonstrated to be effective. Since wood has fewer flexibility and comfort demands than cotton, there is also a greater tendency to incorporate inorganic treatments to reduce wood flammability.<sup>16</sup> Flame-retardant treatments

for wood must consider carefully the end use. For example, flooring has high durability demands, while fencing or building siding will have higher demands for weathering and UV exposure. As with textiles, there is a strong existing market for surface treatments of wood, such as varnishes, paints, and even pressure treatments to impregnate wood with materials to prevent rot. Due to this existing infrastructure, it is ideal if surface treatments to reduce wood flammability are compatible with these technologies.

#### 14.1.1.3 Foam

The United States alone produces over 1.9 million metric tons of polyurethane foam annually, split nearly evenly between rigid and flexible types.<sup>17</sup> Furniture and bedding account for over half of all flexible foam production, with the bulk of the remainder going to transportation. These materials are now ubiquitous in homes as furnishings and bedding, and in the transportation sector where they are used most heavily for seating. Polyurethane foams exhibit a high heat release rate (HRR) after ignition and produce a large amount of especially toxic smoke.<sup>18</sup> In addition, during combustion polyurethane foams tend to aggressively melt-drip, which can contribute to flame spread and flash-over events. Coatings serves as a good means of imparting fire resistance to foams owing to their high surface area and porosity. Because of foam's tendency to melt-drip, foam FR coatings tend to focus first on providing structural support. This is often in the form of a ceramic treatment or shell and can sometimes be paired with other chemistries to slow and/or reduce heat release as the foam degrades. Due to the high levels of smoke release by most polyurethane foams, reduction of smoke release is especially important. Please see Chapter 31 of this book for more information on flammability and fire protection of foam materials.

Unlike textiles and wood, there are not currently commonplace coating technologies in use for foam. Due to their compressibility, conformal coatings can be applied to flexible foams, followed by manual expulsion of the solution carrying the coating materials. Rigid foams present a greater challenge and are not as amenable to coating treatments. The implementation of flow-through technologies could offer an automated way to coat foam at an industrial scale. Even so, the sheer volume of solution paired with the time and energy costs of drying coated foams have acted as a barrier to commercial implementation of many solution-based coating technologies for foam.

## 14.2 LAYER-BY-LAYER TREATMENTS

Layer-by-layer (LbL) assembly represents an interesting technique for the design and deposition of functional coatings and membranes. The fundamental concepts of this technique were disclosed in 1966 by Iler who reported the deposition of oppositely charged micro particles on glass.<sup>19</sup> Despite this early work, the practical application of the LbL was only realized decades later by Decher.<sup>20</sup> Since then, the LbL technique has been successfully applied in many

research fields including the deposition of FR coatings.<sup>21,22</sup> Through the years, this multilayered deposition has proved to be an excellent FR strategy, as demonstrated by high number of published papers as well as by the many reviews available on this topic.<sup>3,23–26</sup> Within this context, this section is aimed at providing the fundamental operating principles of the technique and the most interesting FR results achieved on different substrates.

#### 14.2.1 PRACTICAL CONSIDERATIONS OF LAYER-BY-LAYER ASSEMBLED FLAME-RETARDANT TREATMENTS

LbL assembly results in multilayered coatings by exploiting one or more interactions occurring between selected components in a specific solvent.<sup>22</sup> Although many possibilities exist (e.g., hydrophobic interactions, donor/acceptor interactions, or specific recognition), up to now most of the LbL assemblies have been fabricated through the electrostatic attraction that occurs between polyelectrolytes (PE) or nanoparticles (NP) in water.<sup>27</sup> A typical deposition procedure encompassing for example a positive PE and a negative NP can be performed by alternately dipping the substrate in the PE and NP containing aqueous solutions/suspensions (Figure 14.1). A rinsing step is normally performed in order to remove the excess PE before transferring the substrate into the NP suspension. A final rinsing step completes the deposition cycle. During each deposition step, polyanion-polycation complexes are formed at the substrate/water interface with an overall surface charge reversal that depends on the charge of the deposition bath.<sup>28</sup> By repeating these steps multiple times, a multilayered coating with controlled thickness and composition is generated.

The number of interacting layers within the assembly repetitive unit (deposited in a single cycle) is conventionally referred to as bilayer (BL), trilayer (TL), or quadlayer (QL) when two, three, or four components are employed, respectively. The chemistry of the selected components, the concentration, the pH, the ionic strength, temperature, and time are the main parameters controlling the outcome of the deposition.<sup>22</sup> This produces broad processing windows where it is always possible to find the conditions that allow for an optimal film build-up once the constituents have been identified. Thanks to this design freedom, the development of LbL nanocoatings in the field of flame retardancy started off by assembling components capable of mimicking the main FR action of conventional systems such as polymer nanocomposites and intumescent coatings.<sup>29–32</sup> Indeed, both systems can achieve substantial FR results by producing, during combustion, a protective barrier capable of limiting the mass/heat transfer from/to the flame. By combining synthetic or natural polyelectrolytes (e.g., polyethylenimine (PEI), chitosan (CS), etc.) with nanoparticles of different shapes (e.g., silica nanospheres (SNP), halloysite nanotubes (HN), montmorillonite nanoplatelets (MMT), etc.), it is possible to assemble a nanoparticle rich layer similar to the one produced during combustion by

polymer-clay nanocomposites.<sup>29</sup> Similarly, if the nanoparticles are replaced by phosphate containing polyelectrolytes (e.g., ammonium polyphosphate (APP) and poly(sodium phosphate) (PSP, sometimes referred to as sodium hexametaphosphate)), it is possible to deposit assemblies with micro-intumescent features.<sup>32</sup>

To state that the FR LbL coatings fall in either one of the two described FR archetypes would be a great limitation. There are indeed many other classes of materials that can be incorporated within an LbL coating such as carbon-related materials (e.g., nanotubes, nanographites, graphenes, etc.), biomacromolecules (e.g., nucleic acids, proteins, etc.), and MXenes (a novel broad family of two-dimensional carbides and nitrides of transition metals).<sup>22</sup> With such a broad selection of components, it is possible to investigate different hybrid FR mechanisms as well as include additional functional characteristics such as super-hydrophobicity, electrical conductivity, and anti-bacterial properties.<sup>33–36</sup>

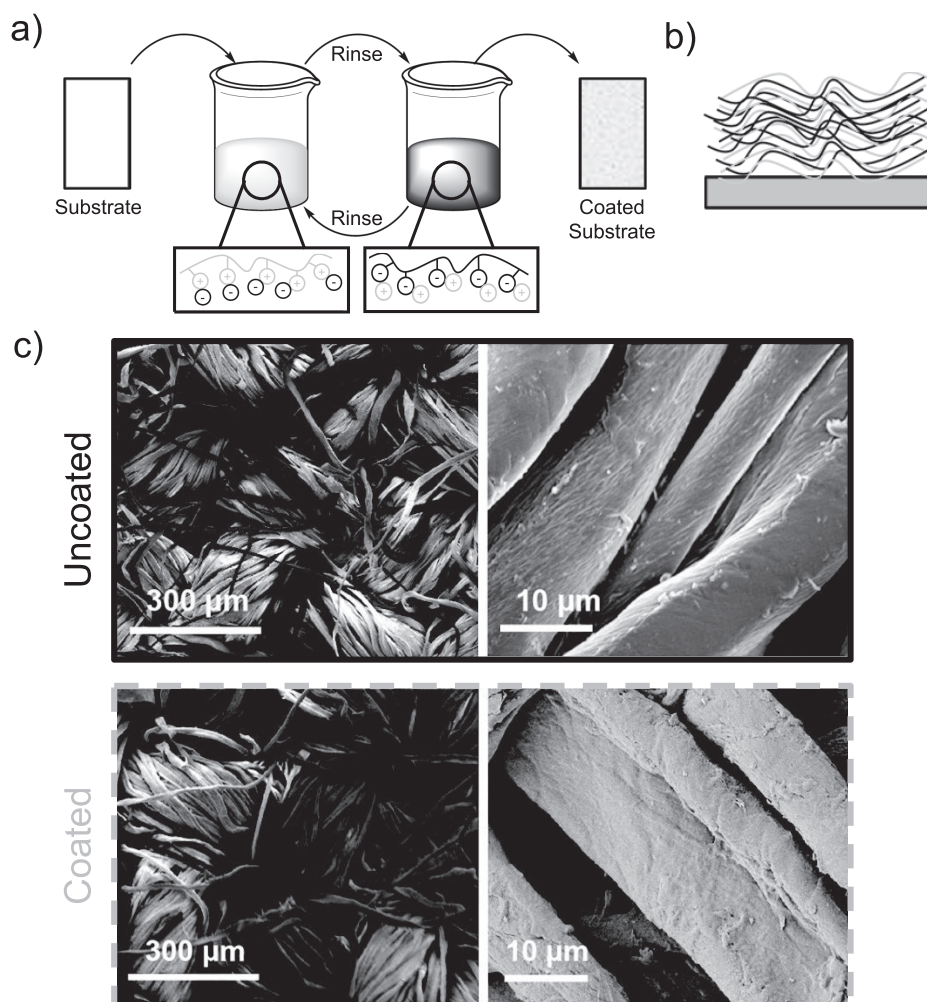
Up to now, dipping has been the most widely used approach to deposit FR LbL coatings. This is linked to the ease and accessibility of this method that represents the most studied choice for the assembly of LbL coatings in all research fields. Laboratory scale dipping methods can be easily scaled up to industrial pad-dry processing equipment and maintain coating performance.<sup>37,38</sup> In an effort to speed up the processing time, spray-assisted LbL deposition has also been demonstrated as viable option to deposit functional coatings on various substrates.<sup>39–41</sup> Contrary to the conventional dipping procedure, this latter approach is relatively new, and more work is needed in regard to the fundamental aspects of the process.

#### 14.2.2 USE-CASES OF LAYER-BY-LAYER ASSEMBLED FLAME-RETARDANT COATINGS

Here we discuss the most efficient FR LbL treatments for textiles, foams, and other substrates. Examples were chosen based on the achieved FR performances, the adopted FR mechanism, and the particular features of the assembled LbL coating (e.g., first use of a certain chemical/FR mechanism/deposition approach, implementation of multifunctional characteristics, etc.).

##### 14.2.2.1 Textiles

Textiles (natural, synthetic, and blends) were the first substrates to be coated using layer-by-layer assembly for flame retardant purposes. This can be linked to the already existing surface approaches and industrial-scale equipment conventionally employed to improve their FR properties. Indeed, the direct impregnation of the FR chemical represent the only options to confer FR properties to natural fabrics such as cotton, ramie, silk, and wool.<sup>42</sup> Synthetic fabrics such as PET, PA, and polyacrylonitrile (PAN) might also rely on additional approaches, such as the bulk inclusion of the FR additive during melt- or wet-processing and the copolymerization of FR monomer within the polymer chain.<sup>43</sup> These



**FIGURE 14.1** (a) Schematic of layer-by-layer assembly, where a substrate is first dipped into a solution containing a charged polymer (here shown as a polycation), followed by a rinse step and then immersion in a solution containing the oppositely charged polymer. (b) Cross-section cartoon showing the deposited coating atop a substrate. Interdiffusion between deposited polyelectrolytes is common, as shown here. (c) Scanning electron microscope images highlight the conformal nature of a CS/PSP coating on cotton fabric. The fibrous structure of the textile is preserved after coating even at the microscopic scale. Adapted from Ref. <sup>44</sup> with permission.

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latter approaches suffer from constraints such as limited processability and decreased mechanical properties of the produced fibers. From this point of view LbL conformal coatings represent a viable choice as the treatment does not affect the fiber production outcome. Electron microscope images, such as those displayed in Figure 14.1c, highlight the conformal nature of LbL coatings, with treated fabric appearing nearly indistinguishable from untreated. If designed correctly, an LbL treatment should not modify the main fabric features related to mechanical and optical properties (i.e., comfort and design).<sup>44</sup> This is thanks to the already mentioned versatility (materials choice and processing parameters) of the LbL approach that allow for the proper design of the coating depending on the substrate of choice and the desired functional properties. Indeed, although there are some studies reporting a singular LbL treatment capable of conferring FR properties to

cotton, PET, and their blend (i.e., PECO), the most efficient approach is to select the coating constituents and FR action in order to match the chemistry and burning behavior of the fabric.<sup>45</sup> To this end, coating formulations based on the concept of intumescence have proved most effective on natural fabrics such as cotton and ramie.

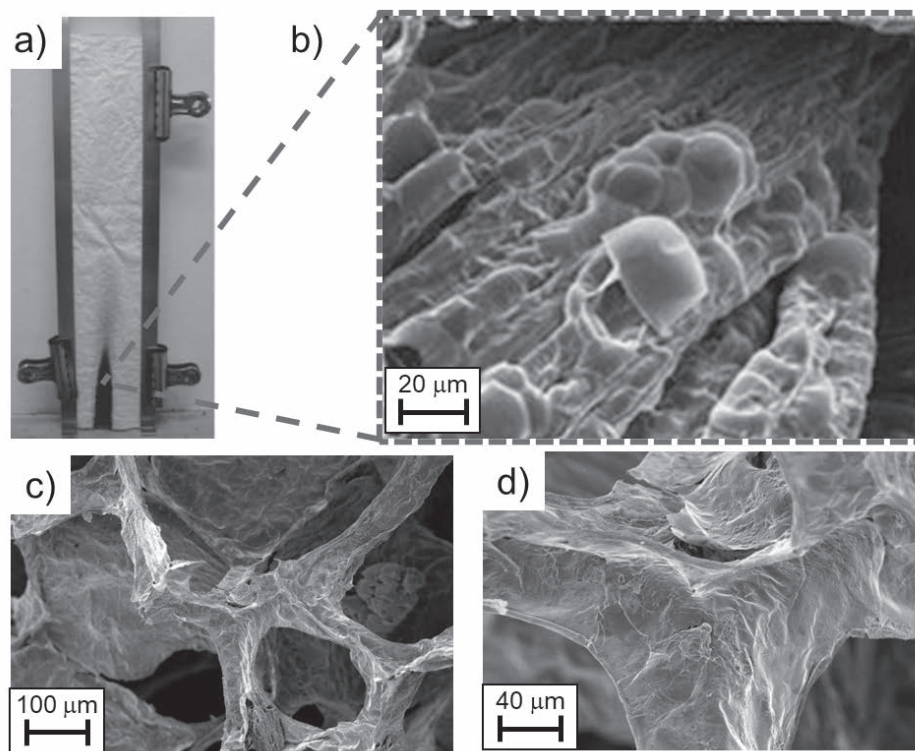
Intumescent-like formulations can be easily assembled in a BL fashion by combining polyphosphates (e.g., polyphosphoric acid PPA, APP, and PSP) with either synthetic or natural polyelectrolytes (e.g., polyethylenimine (PEI), chitosan (CS), or starch (ST)).<sup>46–49</sup> The polyanions act as the acid source, while the polycations act as the carbon source. The foaming agent, the third component of an intumescent formulation, is produced upon decomposition of the coating components. For example, ammonia can be released from either unexchanged ammonium ions in APP or the amino groups of CS.<sup>50</sup> Decomposition products coming

from the polycation can also contribute to the formation of an expanded protective structure. A landmark article was published in 2011 by Li et al. where poly(allylamine) PAH was combined with PSP on cotton fabric.<sup>46</sup> A 20 BL coating imparted self-extinguishing behavior in a vertical flame spread test (VFST, ASTM D6413) and dramatically increased the amount of char produced upon cotton decomposition. The formation of micron-scale intumescent like structures was confirmed by post combustion residue SEM observations (Figure 14.2). Interestingly, the same PAH/PSP coating did not produce expanded structures when deposited at 10 BL, indicating that an intumescent system requires a minimum coating thickness in order to properly display its FR action. Similar FR results were achieved on ramie fabrics by using PEI and APP.<sup>48</sup> This system was deposited by either conventional dipping or spray, highlighting how the latter can reduce the number of BL required to achieve the desired FR properties to 10–15, while also reducing the overall processing time.<sup>51</sup> The durability of the coating and its FR properties to laundering represents an additional challenge for waterborne LbL coating.

In order to address the washing problem, different strategies can be exploited. For example, the inclusion of a UV-curable latex in an intumescent formulation based on CH and APP has been shown to improve the durability of

the coating while maintaining good FR properties.<sup>49</sup> After photo-curing, a 3 BL coating exhibits self-extinguishing behavior in a horizontal flame spread test (HFST) after washing for 1h at 65°C. More recently, LbL coatings durable to 50 washing cycles (AATCC 143–2014 method) have been produced by assembling phenylphosphonic acid (PHA) and 3-aminopropyltriethoxysilane (APTES) on polydopamine (PDA)-coated cotton.<sup>52</sup> Fully renewable intumescent-like LbL coatings can also be assembled by replacing the synthetic acid source with bio-macromolecules such as deoxyribonucleic acid (DNA), caseins (CA), vitamins, and phytic acid (PhA).<sup>53–56</sup> PhA has been recently used to create a high performing intumescent treatment deposited on cotton.<sup>57,58</sup> For example, PEI/melamine and PhA can self-extinguish in a vertical flame test with only 4 BL deposited. When post treated with a diluted solution of poly(dimethylsiloxane) (PDMS), the coated fabric also achieves good water repellent behavior.<sup>58</sup>

In parallel to synthetic or natural polyelectrolytes, nanoparticles have also been explored in FR assemblies. As far as FR properties are concerned, although nanoparticle-based LbL coatings were first to be investigated on cotton, the achieved results were limited compared with intumescent assemblies.<sup>59,60</sup> Hybrid coatings encompassing both approaches have recently demonstrated efficacy when the selected nanoparticle is employed as mechanical



**FIGURE 14.2** (a) Image of cotton fabric coated with an intumescent LbL film after vertical flame testing (ASTM D6413). (b) Inset shows the micro-intumescent effect, which yields self-extinguishing behavior and protects the fabric from further damage by fire. (c) Example of a nanoparticle-based LbL coating preserving the structure of open cell polyurethane foam after fire testing. (d) Electron micrograph showing struts of the foam are hollowed out, leaving an empty shell of graphitic material behind. Parts (a,b) adapted from Ref. <sup>46</sup>.

reinforcement of the produced intumescent structure.<sup>61</sup> Besides improving the FR properties, the use of nanoparticles can provide additional properties to the deposited coating. For example, the use of Ag nanowires in combination with a PEI/PhA assembly has shown both self-extinguishing behavior and EMI shielding characteristics on cotton fabric.<sup>62</sup>

As far as synthetic fabrics are concerned, PET represents the most coated substrate followed by PA and PAN. LbL coatings designed for these fabrics must consider their inherently different burning behavior with respect to natural ones. Indeed, the melting processes that occur during combustion can have detrimental effects on the ability of the coating to produce a protective barrier and thus its overall FR behavior.<sup>63</sup> For these reasons, the compositions of most of the LbL coatings developed for synthetic fabrics differ significantly from those already discussed for natural ones. This peculiarity is certainly highlighted by the results achieved by one of the first FR LbL assemblies developed for PET.<sup>64</sup> Similar to early attempts on cotton, nanoparticles were employed to achieve a result typical of polymer nanocomposites.<sup>60</sup> Positively charged alumina coated silica and negatively charged silica were assembled on PET fabric. A 5 BL coating achieved self-extinguishing behavior in VFST, while also prolonging the time required to ignite the fabric during cone calorimetry tests (35 kW/m<sup>2</sup>).<sup>64</sup> Interestingly, the increase in BL number did not produce additional benefit as the increased thickness of the deposited coating led to its instability during combustion due to the synthetic fiber melting. Spray assisted deposition of this silica/silica LbL was also attempted on PET mats (density 490 g/m<sup>2</sup>).<sup>65</sup> Horizontal and vertical spray configurations were also investigated, highlighting the former as the most efficient, as supported by a dedicated study on cotton.<sup>41</sup> When compared, the results achieved by horizontal spray deposition on both cotton and PET confirms the good FR potential of nanoparticles for synthetic fabrics.

Despite the good results achieved, a major problem of nanoparticle-based coatings is poor washing durability. To address this issue, polyelectrolytes can be used with different cross-linking strategies that can be applied to reduce the coating's swelling in water. Cross-linked polysaccharide-based coatings have been developed with either an improved char forming ability or an intumescent behavior.<sup>66–68</sup> The assembly of CS with sodium alginate (SA) and Cu<sup>2+</sup> ions on PET produces dense charred residues capable of preventing melt-dripping and self-extinguishing the flame during VFST with just 2 QL deposited.<sup>66</sup> Similarly, Pan et al. exploited partially oxidized SA in combination with PEI and a post cross-linking treatment with hypophosphorous acid on PET fabric subjected to a UV-grafting pretreatment.<sup>67</sup> Fabric treated with 15 BL are capable of self-extinguishing the flame during HFST even after 12 laundering cycles (GB/T 17595–1998).

Intumescent-like assemblies have been achieved by including a phosphate containing component such as APP

or PhA.<sup>68–70</sup> When deposited on PET, 10 BL of a CS/APP assembly can only suppress the melt-dripping phenomenon without being able to stop flame spread during flammability tests.<sup>69</sup> This deficiency can be remedied to achieve self-extinguishing behavior by including guanidine sulfamate within the CS solution, without increasing the number of deposited BL.<sup>69</sup> Similarly, a QL architecture encompassing PhA, CS, and SA deposited on PA66 fabric can achieve a UL-94 V1 classification with only 5 QL (i.e., 20 deposition steps), whereas only 5BL of a CH/PhA assembly (i.e., 10 deposition steps) are required to reach the same classification.<sup>71,72</sup> This difference can be ascribed to the increase in PhA content within the coating when moving from a QL to a BL architecture. In addition, the CS/PhA assembly also exhibits durable FR properties (5 washing cycles according to AATCC test method 61(2A)-1996) when post cross-linked with sodium tetraborate decahydrate.<sup>72</sup>

PET and PA fibers are also typically employed in blends with cotton in order to target specific characteristics such as durability, reduced cost, and comfort.<sup>73</sup> From an FR point of view, this further complicates the task as blends tends to combine the weakness of their components (e.g., ignitability of natural fibers and melting of synthetic fibers).<sup>74</sup> The best way to address this problem seems to be the use of intumescent-like formulations or hybrid coatings based on Si-P interactions.<sup>75–77</sup> For example, a CS/PhA coating assembled at 15BL was reported to impart self-extinguishing behavior to PECO during VFST (ASTM D6413).<sup>75</sup> Similar results were achieved when 15 QL encompassing CS, TA, and PhA were deposited on NYCO.<sup>78</sup> It should be noted that the number of deposition steps required to achieve satisfactory results on blends is, on average, higher than those related to a single fabric type (e.g., 15 BL vs 5 BL for PECO vs PET, respectively). This observation further highlights the challenges associated with textile blends. Besides PET and PA, studies have been performed on PAN fabrics as well.<sup>79</sup> Coatings encompassing silica precursors and phosphate-containing components have been developed achieving a hybrid FR effect.<sup>80</sup>

#### 14.2.2.2 Foams

A few years after the publication of the first studies dealing with FR LbL coated fabric, a study reported of a LbL coating capable of reducing heat release rates of open cell flexible polyurethane foam (PUF).<sup>81</sup> The study of PUF has been growing ever since and has formed a significant enough body of research to have a review solely on this topic.<sup>82</sup> Polyurethane foam has a favorable surface/bulk ratio and the open cells allow for an efficient and straightforward deposition of a LbL coating. Indeed, each solution/dispersion can easily penetrate inside the 3D structure of the foam and eventually yield a continuous coating that extends through the entire volume of the foam.<sup>83</sup> The well-known structural collapse of polyurethane foam is often considered one of the most dangerous phenomena at the early stages of a developing fire and, as a consequence, has been a key target of FR LbL assemblies.<sup>84</sup>

Melt-dripping suppression and conspicuous HRR reduction is normally observed if the performed surface modification is capable of either delaying or preventing foam collapse. The literature suggests that the best way to achieve this is by depositing a nanoparticle-based assembly, where the presence of nanoparticles is likely to provide the mechanical strength required to withstand the foam collapsing (Figure 14.2).<sup>23</sup> The plethora of LbL coatings developed up to now can be roughly classified according to the shape/aspect ratio of the nanoparticle employed: spherical, needle-like, and platelet-like. While the last two categories have been widely investigated, very few studies use spherical nanoparticles,<sup>85–87</sup> which might be linked to a reduced FR efficiency with respect to aspect ratio. The deposition of needle-like particles such as sepiolite rods, halloysite, and titanate nanotubes in combination, paired with different polyelectrolytes, has shown effective reductions in combustion rates and smoke production during cone calorimetry tests.<sup>88–90</sup>

Indeed, the dense fibrous network resulting from LbL deposition has proven capable of preventing foam collapsing. Additionally, combustible volatiles can be either trapped by the tubular structure of the nanoparticles or diluted over time as they have to pass through a dense inorganic fibrous network.<sup>90</sup> The use of multi-walled carbon nanotubes (MWCNT) clearly demonstrates these two FR effects.<sup>91,92</sup> MWCNT can be dispersed in water by employing stabilizing polyelectrolytes such as pyrene functionalized-PEI and PAA.<sup>91</sup> The resulting dispersions are then capable of yielding steady LbL growth, where the MWCNT are found embedded within a PEI/PAA matrix. From a flame retardant point of view, foam coated with 9 BL self-extinguishes the flame in VFST while also achieving 67% and 80% reductions in pkHRR and TSR, respectively by cone calorimetry (35 kW/m<sup>2</sup>). It is important to note that this performance represents FR properties seldom achieved by other LbL systems. A recent work exploited silver microwires to simultaneously achieve FR and EMI shielding properties, further highlighting the versatility of these multilayered coatings in delivering multifunctional properties.<sup>93</sup>

Nanoplatelets are the most common morphology of nanoparticles employed in FR LbL coatings applied to polyurethane foam.<sup>23</sup> This is related to their shape that, during LbL deposition with a polyelectrolyte, forces them to assemble parallel to the surface of the substrate, recreating a nacre-like or brick and mortar (“nanobrick wall”) structure that is well-known for its FR behavior.<sup>94</sup> An early study demonstrated the potential of this structure by employing chitosan and montmorillonite (MMT) clay.<sup>95</sup> The resulting stratified coating produced a 52% reduction in pkHRR in cone calorimetry testing at a flux of 35 kW/m<sup>2</sup>. The use of MMT-based coatings was also evaluated in a large scale test with promising results.<sup>96</sup> The influence of different platelet sizes has been investigated, highlighting how high aspect ratio particles can achieve the best FR performance due to the increased probability of particle

overlapping even when few bilayers are deposited.<sup>97,98</sup> This is clearly shown in a study where a direct comparison between MMT and the larger diameter vermiculite (VMT) has been performed, with the latter performing best, even with only 1 or 2 deposited BL.<sup>97</sup> Within this context, the use of graphene-related materials such as graphene oxide nanoplatelets (GO) produced interesting results.<sup>99,100</sup> In particular, the use of GO in combination with either CS or poly(diallyldimethylammonium chloride) (PDAC) has been shown to influence the release of volatiles to the point of reaching a non-igniting behavior during cone calorimetry tests (35 kW/m<sup>2</sup>).<sup>101,102</sup> The 6 BL PDAC/GO coatings assembled in the presence of a phosphate salt, as an ionic strength modifier, exhibit heat-shielding characteristics close to inorganic silica aerogels during flame penetration tests.<sup>102</sup> Recently, MXenes have also been employed with interesting results.<sup>103–105</sup>

Coatings containing only organic polyelectrolytes have also been developed for foam by targeting either a char forming or an intumescent behavior.<sup>106,107</sup> Char forming LbL coatings have been shown to produce substantial FR properties at the expense of a relatively high number of deposited layers (10 BL or 5 QL) when compared with nanoparticle-based coatings. Interestingly, the deposition of intumescent-like formulations was found insufficient to confer FR characteristics to PUF.<sup>108,109</sup> This phenomenon has been related to the early collapsing of the foam structure and its impact on preventing the proper intumescent expansion to occur.<sup>110</sup> A workaround for this problem is the deposition of hybrid coatings encompassing a stacked configuration, where an intumescent system is deposited on top of a nanoparticle containing assembly. Self-extinguishing behavior in HFST and substantial reductions in heat release rates by cone calorimetry can be achieved with systems encompassing either CS/APP or CS/PhA supported by a MMT-rich layer.<sup>111</sup>

By evaluating the literature on PUF it is possible to understand how the research efforts have been primarily directed towards the development of LbL formulations capable of meeting certain FR properties. Particular attention has been paid to reducing the number of deposition steps required for the coating to be effective. There is, however, a limited amount of information on the durability of the deposited coating, where multiple compression cycles and/or wear/abrasion processes occur. A few studies highlight how an LbL coating cracks but does not detach from the surface of PUF upon multiple deformations when a proper adhesion between the substrate and the coating is achieved.<sup>112,113</sup> Despite being cracked, the deposited coating remains flame retardant. Within this context, the plasticizing effect of water must be considered. It has been indeed demonstrated that damaged LbL coatings might display self-healing characteristics when exposed to a high humidity environment with subsequent recovery of functional properties.<sup>114</sup> Self-healing is certainly dependent on the LbL formulation employed and thus should be evaluated systematically for each coating composition.

### 14.2.2.3 Other Substrates

The excellent FR results achieved on textiles and polyurethane foam led to the use of FR LbL coatings on many other substrates. While the number of published papers is not enough to justify a dedicated sub-chapter, it is certainly worth highlighting some of the most interesting papers. In regard to polymer cellular solids, LbL assemblies have been deposited on open cell melamine and silicone foams as well as closed cell PET foam.<sup>115–117</sup> This latter work demonstrated that LbL coatings can be effective on cellular solids even if they are not able to penetrate the internal pores. A 4 QL of an intumescent system encompassing PDAC, PAA, and APP self-extinguishes the flame in HFST and achieves a 25% reduction in pkHRR during cone calorimetry at a flux of 35 kW/m<sup>2</sup>.<sup>117</sup> Cellulose-based materials such as paper, cellulose fiber networks, and nanocellulose aerogels have also been coated by LbL formulations derived from those already employed on natural textiles.<sup>118–120</sup> Of particular interest is the approach employed for the production of FR paper, where the cellulose fibers are LbL-coated before being assembled in the final material.<sup>118</sup> Paper sheets achieving self-extinguishing behavior in HFST were produced with fibers coated with 3.5 BL of a PEI/PSP assembly.<sup>121</sup>

Wet-stable and cross-linked cellulose porous materials made of either nanofibrils or fibers were also LbL modified by flowing the solution/suspension through the open pores of the substrate in a filter-like configuration. This approach turned out to be extremely efficient, producing porous cellulose-based materials characterized by self-extinguishing during HFST and very low HRR (< 100 kW/m<sup>2</sup>) in cone calorimeter testing at a flux of 35 kW/m<sup>2</sup>.<sup>119,120</sup> Thin polymer films (polycarbonate, polystyrene, polylactide, and polyamide), with thicknesses ranging from several hundred microns to a few millimeters, have also been LbL-coated in order to impart FR behavior.<sup>122–125</sup> These film substrates pose the great challenge of having a highly unfavorable surface to bulk ratio. As a major consequence, the thickness of the film has been demonstrated to play a key-role in determining whether the deposited coating can effectively exert an FR effect.<sup>122</sup> Thick samples ( $\geq 1$  mm) would require the deposition of a relatively high number of BL ( $\sim 60$ ) in order to achieve substantial FR properties.<sup>123,124</sup> This problem has been addressed by the implementation of thickening agents such as salts and short chain amines in order to increase the amount of coating deposited per layer.<sup>125</sup> Using this thickening approach, a CS/clay assembly is capable of shielding a 3.2 mm PS film from a flame torch with only 3 BL deposited.

### 14.2.3 OUTLOOK AND FUTURE RESEARCH DIRECTIONS

In just 15 years, LbL assembly applied to the FR field has arisen as one of the most advanced and versatile techniques to impart FR properties to numerous substrates. The favorable processing conditions (room temperature and pressure in aqueous media), and the potential of the coating

ingredients to be either environmentally benign or even biologically sourced, have been the keys to this technique's success. Despite the advantages of having impressive FR properties with an environmentally friendly approach, the high number of deposition steps required to achieve the desired behavior, as well as the production of large volumes of exhausted deposition baths, currently represent the main constraints that are holding back LbL commercialization. Technological and scientific advances are needed to minimize the economic impact of the LbL process, which are currently being addressed by many research groups. The durability of the coating to different stresses (e.g., washing, aging, deformation, and abrasion) must be evaluated and improved. Aside from these practical considerations, it is worth noting how the development of LbL flame retardant treatments introduced the field of fire protection to a number of new chemistries. Before the "LbL era," the properties of polyelectrolyte/nanoparticle complexes in terms of thermal stability and flame retardancy were not known. After years of development, this multilayered technique has also inspired a secondary subfield of preformed polyelectrolyte complexes, which is described in Section 14.3.

## 14.3 POLYELECTROLYTE COMPLEX COATINGS

A frequent criticism levied at layer-by-layer coatings is their very time intensive processing due to the many layers. Depositing a single bilayer in LbL requires at least four liquid exposure steps (one for each solution and its associated rinse), with the possibility of a drying step either in between bilayers or after each rinse. Considering that most published coatings utilize 8–20 BL, the time and energy-intensive nature of the rinse and dry steps have led to research into alternative methods to deposit the charged networks yielded by LbL coatings. Further examination into the fundamental interactions of the charged species in LbL coatings is thus necessary to design improved coatings/processes.

### 14.3.1 CONTROLLING POLYELECTROLYTE COMPLEXATION TO DEPOSIT COATINGS

Polyelectrolyte complexes (PECs) are assemblies of oppositely charged polymers (i.e., polycations and polyanions), whose formation is driven by primarily entropic factors.<sup>126</sup> The individual charged polymeric species exist in an equilibrium with the associated complex that can be tuned by a variety of factors that include salinity, charge density (driven by pH changes), polymer molecular weight, and stoichiometry.<sup>127–131</sup> Many of these parameters can be changed either *ex situ* or *in situ*, yielding control over how, when, and where a complex is formed. The first noted case of a PEC for flame retardancy was in 2014 when delayed complexation was first noticed following inadvertent mixing of two solutions intended for a layer-by-layer film.<sup>132</sup> This initial use-case for the deposition of a single-step PEC was unprecedented at the time, and that work was quickly

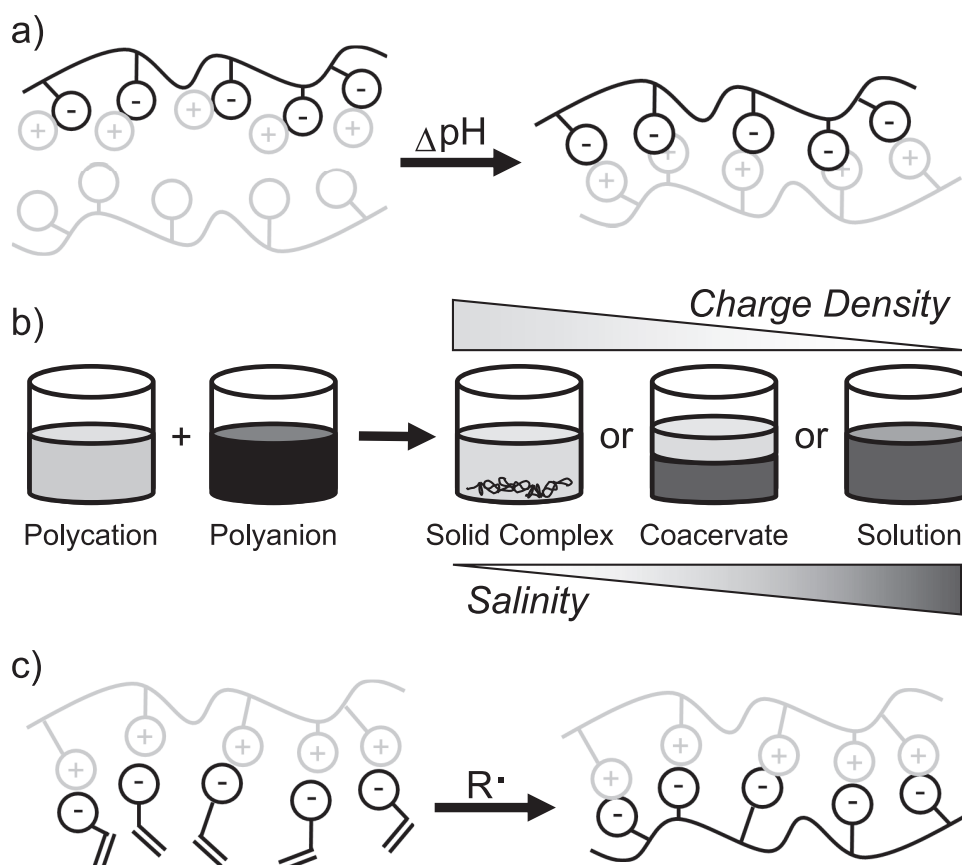


built upon and has yielded a rich field of active research that is described here.

The first class of PEC coatings to be published are what we will describe herein as buffer-cured PECs, demonstrated schematically in Figure 14.3a.<sup>133</sup> In order to replicate the material deposition of layer-by-layer assembled coatings, PEC coatings must begin with significantly higher solution concentrations. A typical LbL coating solution will contain  $\leq 1$  wt% charged species, while PEC coatings often have upwards of 10 wt% solids content. The PEC solution content includes a mixture of cationic and anionic species, at least one of which is a weak (i.e., charge density tied to solution pH) polyelectrolyte. The use of literature pKas enables the preparation of solutions at a pH such that one of the species is uncharged (or at least low enough charge to prevent complexation), removing the driving force for complexation and yielding a “soluble PEC.” After deposition on a substrate and drying, the PEC is then exposed to a buffer that “cures” the PEC, charging the uncharged species while minimally

altering the charge state of the other species. This process yields a complexed film on the substrate that is resistant to rinsing (owing to the water-excluding PEC equilibrium).

Newer classes of PEC treatments have been developed more recently by delving further into methods of tuning the PEC equilibrium. One such example is the use of a flame retardant polyelectrolyte complex coacervate (Figure 14.3b). Polyelectrolyte complexes exist along a continuum of states, being an insoluble complex at one end of the continuum (high charge density and low salinity) or a polymeric solution on the other end (low charge density and/or high salinity). The coacervate phase is a form of liquid-liquid phase separation at moderate charge/salinity that yields the formation of an elastic liquid of high (> 40 wt%) polymer content. This liquid is amenable to bar coating and can then be deposited as a flame retardant treatment on film/sheet-like substrates.<sup>134</sup> The full potential of coacervate treatments has yet to be realized, but they have all of the characteristics to be effective FR treatments at



**FIGURE 14.3** (a) Schematic demonstrating the use of buffer curing to yield a pH-induced change in charge density between two uncomplexed polymers. The result is an insoluble complex that is resistant to water. (b) Schematic of the polyelectrolyte complex-coacervate-solution continuum. At high charge density and low salinity, a solid complex precipitates from solution after mixing. As charge density decreases and/or salinity increases, complexation changes to a liquid-liquid phase separation (coacervation), ultimately yielding a soluble polyelectrolyte solution at very low charge density/very high salinity. (c) Schematic demonstrating how polymerization can be utilized to turn an uncomplexed polycation/monomeric anion pair into a polyelectrolyte complex by polymerizing the monomeric species. Heat or light can be used to initiate the polymerization reaction.

the industrial scale with little modification of existing coating infrastructure. Another emerging class of PEC coating, shown in Figure 14.3c, makes use of polymerization to yield a complex in situ on the surface of a treated material. In this case, a polyelectrolyte is paired with an oppositely charged monomer in solution with a thermal initiator (e.g., potassium persulfate) or a photoinitiator. After deposition of the liquid coating, an external stimulus corresponding to the chosen initiator is applied to polymerize the monomeric component, yielding a polyelectrolyte complex film.<sup>135</sup> Photopolymerization is often a more energy-efficient coating method since heating is not necessary but poses the risk of substrate/coating degradation and incomplete polymerization due to light absorption issues.

### 14.3.2 USE-CASES OF POLYELECTROLYTE COMPLEX FLAME-RETARDANT COATINGS

Polyelectrolyte complex flame retardant coatings have found applications across a wide variety of substrates. Even accounting for the fact that PEC treatments have been an active research area for approximately half as long as layer-by-layer assembled FR treatments, the breadth of PEC FR literature is significantly smaller than LbL. This is likely due to a greater number of constraints (e.g., high concentrations, adjustable charge densities, material cost, etc.) placed on this type of treatment. The following subsections summarize some of the seminal work on flame retardant PEC treatments for a variety of commonly studied substrates.

#### 14.3.2.1 Textiles

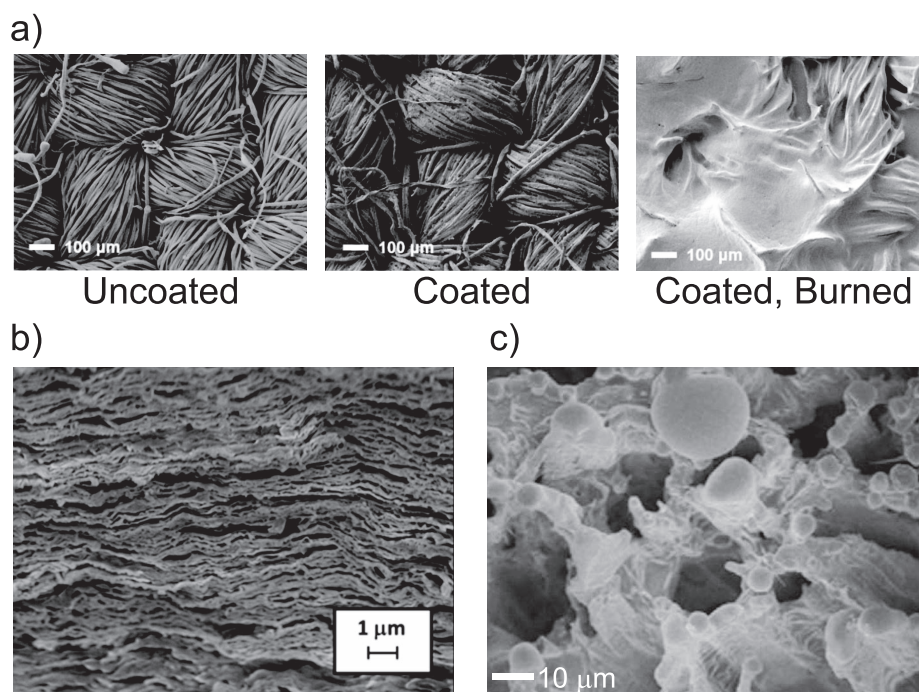
The earliest polyelectrolyte complex coatings were deposited on textiles. As noted previously, the first serendipitous discovery of a “single step” coating represented a significant paradigm shift in the deposition of polyelectrolyte treatments for fire protection.<sup>132</sup> This first treatment mixed polyethyleneimine [PEI] and poly(sodium phosphate) [PSP] and allowed them to complex over time on an immersed fabric substrate. While this time-dependent deposition saved on a number of processing steps, as compared to LbL deposition, the processing time was still considerable and generated a significant amount of waste because the solution was not reusable. Haile et al. later developed a different deposition system where PEI and PSP were mixed at a high pH such that PEI had low charge density.<sup>133</sup> This system could then be complexed through a subsequent buffer curing step after deposition. The buffer curing step is critical to the deposition of an intumescent coating. Without it, there is no acid source for the intumescence process and coated/uncured fabric performs very poorly. The PEI/PSP PEC coating is self-extinguishing through an intumescent-type mechanism in VFST (ASTM D6413).<sup>136</sup> Later work has adopted this technology for nylon-cotton fabric,<sup>137</sup> including wash-durable chemistries,<sup>138,139</sup> and for other natural textiles.<sup>140</sup>

More recent iterations of buffer cured PECs have made use of additives, to either the polymer solutions or to the

buffers.<sup>141</sup> On nylon-cotton fabric, it was found that the incorporation of a melamine deposition step prior to the ultimate buffer curing of the PEC could yield self-extinguishing behavior after forming melamine polyphosphate in situ (Figure 14.4a).<sup>137</sup> The melamine-containing PEC coating is self-extinguishing in VFST (ASTM D6413) and exhibits a negative pyrolytic energy balance in differential scanning calorimetry. Importantly, the incorporation of metal ions affects PEC interactions and thus can enable tunable viscosity, which is important for controlling weight gain and processability.<sup>141,142</sup> Other studies have included inorganic clays in PEC-style motifs to protect high heat release textiles that lack the char-forming potential of cotton, such as acrylic fabric.<sup>143</sup> In this study, Carosio et al. developed a chitosan/montmorillonite treatment that formed a complexed gel that could be applied via blade coating. Despite not using LbL processing, this coating exhibited the nanobrick wall structure common to LbL treatments (Figure 14.4b), which allows the coating to act as an effective thermal barrier and reduce flammability. More recent work has sought to increase the breadth of available chemistries (e.g., inclusion of biomolecules) and incorporate multifunctionality, such as water repellency, to the PEC coating on fabric.<sup>144–146</sup>

#### 14.3.2.2 Foams

As noted throughout the discussion of layer-by-layer treatments, flame retardants for polyurethane foam most often requires a high percentage of inorganic content to counteract its high heat release and tendency to form fire-spreading melt pools. The need for inorganic content poses a challenge for most PEC-based FR treatments since the single-step deposition requires a generally much higher concentration of dissolved solids. Clays and other inorganic species are challenging to load to 10+ wt% in solution due to their large size and poor stability. To date, very little published work exists that successfully reduces foam flammability using PEC treatments. Conveniently, polyphosphates have long been known to act as deflocculants/dispersants for a variety of inorganic particles.<sup>147</sup> Since polyphosphates like APP and PSP have good utility as FR agents, it seems natural to pair them for improved clay loading in PEC FR treatments. The first work to pursue this line of reasoning made use of the strong ability of polyphosphates to stabilize halloysite to prepare clay/polyelectrolyte solutions with a very high clay loading.<sup>148</sup> This clay allowed both improved fire resistance by the PEC/clay system, but also counteracted the pure intumescent PEC's tendency to increase the degrading foam's smoke production through the sequestration mechanisms noted in the LbL subsection. The halloysite-filled PEC system reduced the  $pkHRR$  of foam by 53% (35 kW/m<sup>2</sup>) and reduced the total smoke release (TSR) by 17% compared to the unfilled PEC, although it still had a higher TSR than neat foam. A similar work utilized graphene oxide (GO) deposited as a second step after coating the foam in an intumescent PEC precursor solution.<sup>149</sup> Thermal reduction of the GO layer led to improved char yield and fire protection, with coated foam passing a vertical burning test



**FIGURE 14.4** (a) Scanning electron microscope (SEM) images of uncoated nylon-cotton, NYCO coated with a melamine-containing PEC, and the coated NYCO after vertical flame testing, respectively. Despite utilizing high concentrations, PEC coatings remain highly conformal to their substrate. (b) Cross-sectional SEM image of a chitosan/montmorillonite PEC coating on acrylic fabric. The coating self-stratifies into a layered structure after blade coating. (c) Image of a PEC-coated wood article following fire exposure. Much like cotton fabric, wood's charring nature leads to a microintumescent effect with polyamine/polyphosphate PEC treatments. Part (a) reproduced from Ref. <sup>137</sup> with permission, part (b) reproduced from Ref. <sup>143</sup> under a creative commons license, and part (c) reproduced from Ref. <sup>151</sup> with permission.

AuQ13

(TB 117–2000). The dynamic nature of PEC ionic bonding yielded a coating that was also found to be self-healing.

#### 14.3.2.3 Wood

The processing advantages of PEC coatings has been most pronounced and widespread in wood. As mentioned previously, wood's complex surface yields extremely slow rates of diffusion and adsorption. As a result, traditional polyelectrolyte treatments making use of LbL deposition take prohibitively long to deposit.<sup>150</sup> The influence of immersion time on the deposition of buffer cured PECs was investigated on wood and yielded self-extinguishing wood articles through an intumescent polyelectrolyte complex system (Figure 14.4c).<sup>151</sup> It was found that the diffusion front of the curing buffer could carry the coating further inside the wood, ultimately leading to a 1 mm depth of penetration. Treatment time remains a challenge because of diffusion of polymeric species and buffer into the bulk of the wood. Pressure treatment with buffer cured PECs dramatically reduces processing time, representing an important step toward the commercialization of polyelectrolyte FR technologies for wood.<sup>152</sup>

A critical flaw in the deposition of buffer-cured PECs is their reliance on diffusion to deposit a coating. While this is unavoidable for the flame retardant species, diffusion of

a buffer to cure the complex presents a time barrier that diminishes the potential of PECs for wood fire protection. Recent efforts have turned towards photopolymerization and coacervates to further reduce immersion steps.<sup>135,153</sup> In the case of photopolymerization, a monomeric phosphate was paired with a cationic polymer and post-deposition photopolymerization formed the complex on the surface of the wood. Despite the short penetration depth of the UV light, early studies indicate that the coated material is “sealed” by the polymerization of the exterior material.<sup>135,154</sup> The photopolymerized PEC treatments were more effective on plywood, where they exhibited a  $pkHRR$  decrease of nearly 50% (at a flux of 35 kW/m<sup>2</sup>). Further chemical alterations will need to be investigated to determine optimal treatment conditions for other forms of wood. Although significantly less common in the literature, the use of coacervates as a flame retardant treatment allow for truly single-step deposition of a flame retardant coating. A similar coacervation approach was also recently used to flame retard paper in a single step.<sup>134</sup>

#### 14.3.3 OUTLOOK AND FUTURE RESEARCH DIRECTIONS

Since their discovery a decade ago, polyelectrolyte complex treatments for fire protection have rapidly matched the performance of layer-by-layer systems, while requiring

significantly fewer processing steps. While many promising steps have been taken toward commercializing PECs, future work must seek to understand and address the lingering questions/flaws associated with these treatments. First, the “potlife” of the deposition solutions must be evaluated. As noted previously, PEC deposition solutions are significantly (up to 10×) more concentrated than those used for LbL deposition. Treatments must remain effective after numerous deposition cycles to avoid waste and ensure economic viability of these coatings. Second, the field should continue investing in ultraviolet curing. The buffers utilized for curing PEC treatments are prone to fouling and generate a large amount of solution waste. Switching to UV-based curing approaches will avoid an immersion/drying step and generate less waste. Finally, as with LbL systems, the durability of these treatments to washing/weathering for textiles and wood, respectively, must be assessed. While the field is still young, PEC-based approaches hold significant promise for flame retardant treatments that are environmentally benign and scalable for widespread implementation.

## 14.4 SOL-GEL COATINGS

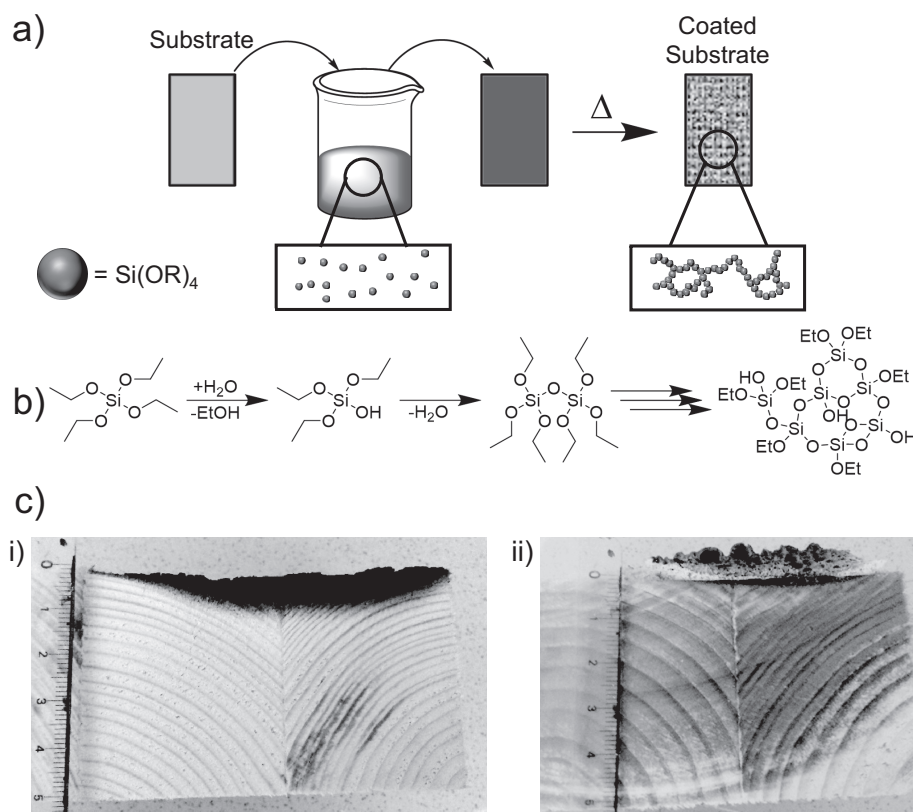
The sol-gel process provides a wet-chemical route for the synthesis of either inorganic or hybrid organic–inorganic chemical structures.<sup>155</sup> Very generally, hydrolysis and polycondensation reactions are used to prepare well controlled hybrid materials with a broad selection of processing routes and parameters.<sup>156</sup> The sol-gel procedure had been initially developed for the synthesis of homogeneous and pure metal oxide particles.<sup>157</sup> Throughout the years, the technique has been extended to the surface modification of different substrates.<sup>158–160</sup> The intrinsic fire retardant characteristics of sol-gel coatings have been known since the nineties, as evidenced by patents focusing on the production of composite coatings for patching/sealing of substrates.<sup>161</sup> Sol-gel based FR coatings for porous materials (e.g., synthetic and natural woven and nonwoven fabrics, fibers etc.) were demonstrated in the early 2000s.<sup>162</sup> During the past two decades, the sol-gel technique has been widely developed in the field of FR coatings capable of meeting increasingly demanding fire safety criteria.<sup>3,163,164</sup>

### 14.4.1 SOL-GEL CHEMISTRY

In a sol-gel process a colloidal solution (“sol”) is obtained starting from liquid precursors. This is commonly achieved through hydrolysis and condensation reactions of metal alkoxide precursors, although a sol can be generally linked to a colloidal system to encompass different systems under the general “sol-gel” term.<sup>155</sup> The so produced “sol” can be further developed into a network structure (“gel”) defined as non-fluid 3D network that extends through a fluid phase (Figure 14.5). Gels can be grouped into five classes that are relevant in the sol-gel synthesis of materials: colloidal, metal-oxane polymer, metal complex, polymer complex

I, and polymer complex II.<sup>165</sup> The polymer complexes are classified based on the type of bonding occurring between the polymers. The sol-gel chemistry was first reported in the 19th century when a gel was produced from a silicon alkoxide through hydrolysis and condensation reactions favored by atmospheric moisture.<sup>166</sup> This general concept has been widely employed and investigated through years by exploiting, for example, acid or base catalysis in order to form gels with different structures. Although this hydrolysis and condensation chemistry, often referred as “traditional sol-gel chemistry,” presents some limitations (e.g., high reactivity of the precursors and phase separation when combining precursor with different rates of hydrolysis), it still represents the most widely used sol-gel approach in the field of materials chemistry. Here we will focus on traditional sol-gel that is also the most common employed in the flame retardant field.

Metal alkoxides are the most commonly employed reactants for sol-gel processes. The most common examples involve the use of transition group metals such as Ti and Zr or p-block elements such as Al and Si. There are, however, many other examples of metal alkoxides produced by different synthesis strategies.<sup>167,168</sup> The ionic character of the M-O bond and the stability of the alkoxy groups can influence the gel structure by affecting the relative rates of hydrolysis and condensation and, eventually, the degree of polymerization.<sup>169</sup> On the other hand, the volatility and viscosity of the alkoxides might affect its suitability for a sol-gel process.<sup>170</sup> Hydrolysis and condensation reactions represent the core of the sol-gel chemistry and are strongly affected by many processes parameters such as the nature of the R group, the water to alkoxide ratio, and the presence of a catalyst.<sup>155</sup> This latter, in the form of either an acid or base catalyst, is needed for the sol-gel chemistry of silica because the reaction carried over at neutral pH is notoriously slow. During hydrolysis, the alkoxy group is replaced by a hydroxyl. The number of alkoxy groups hydrolyzed depends on the reaction conditions and the Si/H<sub>2</sub>O ratio. The subsequent condensation step produces siloxane bonds (or metaloxane bonds for other elements). The degree of hydrolysis, which is affected by pH, has a direct influence on the progression of the condensation. Under basic conditions, hydrolysis is generally completed before the condensation step, whereas in acidic conditions condensation starts before the completion of hydrolysis. The former likely ends up in a colloidal gel, while the latter produces network-like gels. Besides pH, there are other factors controlling the structure of the gel. The presence of solvents in addition to water might enable or improve mixing (many metal alkoxides are not miscible with water) or interact with the metal center. The alkoxide/water ratio is also important as it can be tailored to control hydrolysis. This latter step can be directly influenced by the nature of the R group. In addition to the chemistry linked to gel formation, there are other ways to affect the outcome of a sol-gel process. The drying step is, for instance, capable of impacting the gel structure.<sup>171</sup> Uncontrolled evaporation



**FIGURE 14.5** (a) Schematic of the deposition process for sol-gel coatings. (b) Chemical scheme for the hydrolysis/condensation process that yields a siloxane network. (c) Photos of sol-gel coated wood after single burning item testing, reproduced from Ref. <sup>201</sup> with permission.

produces a collapse of the network into a dense xerogel, which often shows high surface area due to the presence of disordered porosity. Conversely, drying under controlled conditions (e.g., by supercritical drying or freeze-drying) might preserve a large pore volume yielding aerogels or cryogels characterized by low densities.<sup>172–174</sup>

#### 14.4.2 USE-CASES OF SOL-GEL FLAME-RETARDANT COATINGS

With all the abovementioned possibilities, the use of the sol-gel approach in the FR field has been widely studied for almost 20 years. Although conformal coatings represent the majority of the published papers, the use of sol-gel has been also extended to the synthesis of new chemicals or surface modification of particles used for bulk inclusion in polymers.<sup>163</sup> As far as FR coatings are concerned, the first attempts were performed using a traditional sol-gel chemistry (conventional approach). Additives have been included within the formed gel (use of dopants) in order to improve the achieved FR properties. Recently, the synthesis of sol-gel precursors encompassing FR functionality has been proposed.<sup>3</sup> Some of the best performing and unique sol-gel based FR solutions are discussed below.

##### 14.4.2.1 Textiles

As already noted throughout this chapter, textiles represent an optimal starting substrate for the evaluation of coating treatments aimed at FR properties. The first sol-gel treatment with FR properties was attempted on regenerated cellulose fibers using a tetraethylorthosilicate (TEOS) precursor.<sup>175</sup> The treatment produced, under basic conditions, an improved thermal-oxidative stability of the fibers. Subsequently, the influence of different TEOS/water ratios on the FR properties of coatings deposited on cotton, PET, and their blends was evaluated.<sup>176</sup> While the treatment had limited influence on PET fabric, PET-rich blends displayed a remarkable increase in TTI (up to +93%) and a reduction in pkHRR (–34%) in cone calorimetry (at a flux of 35 kW/m<sup>2</sup>). Further studies performed on cotton evaluated the influence of different alkoxy silane or metal-alkoxide precursors, highlighting how TEOS-based sol-gel coatings can achieve the best FR performance in terms of TTI increase and pkHRR and THR reductions.<sup>177</sup> Interestingly, despite the limited reduction in pkHRR when using tetraethylorthotitanate or tetraethylortho-zirconate, and the increase in pkHRR achieved with aluminum isopropylate, a reduction in specific extinction area (i.e., the optical density of smoke per unit mass) and TSR values was observed for all different metal-alkoxide precursors. This result has been ascribed to

the increased water content of the treated fabric as well as the barrier effect exerted by the metal-oxide coating. These preliminary works clearly demonstrated the potential of the sol-gel approach and inspired further developments.

A straightforward way to improve FR properties is represented by the inclusion of FR components within the sol-gel network. The use of phosphorus-based molecules such as ethyl dichlorophosphate or phosphorus acid in a TEOS-based sol-gel process on cotton fabric has been shown to reduce flammability. In particular, the presence of phosphoric acid was found to grant a self-extinguishing behavior during flame tests (TS 5569 EN ISO 6941) with a partial durability to ten washing cycles.<sup>178</sup> Similar results were also achieved on polyacrylonitrile fabric.<sup>179</sup> Commercially available P-based FR formulations and nanoparticles have also been investigated by Alongi and coworkers.<sup>180</sup> AP Exolit® OP1230 (aluminum phosphinate), APMP Exolit® OP1312 (aluminum phosphinate 63.5% by mass, melamine polyphosphate 32% by mass, and zinc and boron oxide 4.5% by mass), and  $\alpha$ -Zirconium dihydrogen phosphate were included within a sol-gel process exploiting tetramethyl orthosilicate (TMOS) as silica precursor. Cotton fabric treated with doped sol-gel coatings required multiple flame applications to achieve ignition. In addition, the inclusion of AP Exolit® OP1230 within a silica network considerably limited the removal of the FR during washing, thus resulting in a semi-durable treatment. Similar properties were achieved with the use of  $\gamma$ -aminopropyltriethoxysilane (APTES) in combination with diethylphosphite.<sup>181</sup> Bio-sourced FR such as phytic acid have also been included in sol gel processes.<sup>35,182,183</sup> When deposited on silk in combination with TEOS, the presence of phytic acid imparts self-extinguishing behavior in vertical flame testing (ASTM D6413–2008).<sup>182</sup> The use of different coupling agents to increase hydrophobicity of the coating imparted wash durability.

The combination of phosphorus-based and nitrogen-based compounds has also been attempted.<sup>184,185</sup> For example, the use of (3-aminopropyl) triethoxysilane doped with phytic acid sol-gel coatings has been shown to confer remarkable FR properties on cotton by achieving a self-extinguishing behavior during flammability tests (ASTM D6413–2008) and LOI values as high as 28.5%.<sup>185</sup> A post-treatment with n-dodecyltrimethoxysilane further endowed the fabric with hydrophobic properties without affecting the FR efficiency. Similar results have been achieved by combining TEOS, hydroxyl-terminated polydimethylsiloxane, and APP on cotton.<sup>186</sup> Besides Si, other metal alkoxides have been evaluated.<sup>187</sup> For example, titanium (IV) butoxide and boric acid (employed with different molar ratios) have been deposited on cotton by a pad/dry/cure process, achieving self-extinguishing behavior during vertical flame tests. In addition, this titania-based coating also produced an increase in hydrophobicity that was not sufficient to impart washing durability. Although the use of doping agents has been demonstrated to improve the FR properties of the treated fabric, this approach might suffer from a poor

compatibility of the doping agent with the adopted sol-gel chemistry. In order to address this problem, recent research has been focused on the modification of the siloxane precursor.<sup>188–190</sup> An early study compared the FR performance of a hybrid precursor with those achievable with a traditional organophosphate. Only the latter solution was capable of self-extinguishing the flame during vertical flammability tests (DIN 53906).<sup>188</sup> Notwithstanding this, the use of a hybrid precursor allowed for a formaldehyde-free process and improved hydrophobicity thus showing the potential for the synthesis of new sol-gel precursors with specific FR functionalization.<sup>191</sup>

More recent work has employed a di-(triethoxysilylpropyl) phenylphosphamide hybrid precursor that produces a self-extinguishing behavior on cotton after prolonged impregnation times. Similar results have been achieved with a 2,2-dimethyl-1,3-propanediol-(3'-triethoxysilanepropyl) phosphoramidate precursor that also produces an increase in LOI (up to 30.1%). Surprisingly, the same treatment produces detrimental results in cone calorimetry (i.e., increased  $pkHRR$  and  $TSR$  values).<sup>189</sup> Conventional FR chemicals have been also modified in order to be exploited in sol-gel chemistry. A 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-modified vinyl trialkoxysilane (DOPO-VTS) has been synthesized and combined with TEOS on PA 6 fibers.<sup>192</sup> There is a synergistic FR effect in the condensed phased resulting in the complete suppression of the melt dripping.

With the FR ability of hybrid sol-gel precursors demonstrated, the next step has been related to the combination of multiple precursors to target multifunctional coatings. For example, 1H,1H,2H,2H-perfluorooctyltriethoxysilane and P,P-diphenyl-N-(3-(trimethoxysilyl)propyl) phosphinic amide have been combined on cotton fabric in order to achieve an FR coating with superhydrophobicity and high oleophobicity, as well as passive antibacterial activity.<sup>193</sup> The use of ionic liquids in combination with sol-gel has also been proposed.<sup>187</sup> The 1-methylimidazolium chloride propyltriethoxysilane and pyridinium chloride propyltriethoxysilane were applied to cotton, followed by a subsequent anion exchange step by dipping the coated fabric in solutions containing hexafluorophosphoric acid, bis(trifluoromethane) sulfonimide lithium, sodium tetrafluoroborate, or sodium acetate. Of all the different counterions evaluated, the hexafluorophosphoric acid was found to provide the optimal FR properties. P,P-diphenyl-N-(3-(triethoxysilyl)propyl) phosphinic amide and the hydrophobic finishing agent polydimethylsiloxane were combined on cotton.<sup>194</sup> The so treated fabrics achieved a self-extinguishing behavior during vertical flame testing (GB/T 5455–1997), while also displaying superhydrophobic, self-cleaning, and abrasion resistance properties.

#### 14.4.2.2 Other Substrates

Following the good results achieved on textiles, the sol-gel approach has been extended to other substrates such as polymeric foam and wood. An early study by Bellayer et al.

designed a sol-gel formulation encompassing tetraethoxysilane, methyltriethoxysilane, 3-aminopropyl triethoxysilane, and diethyl phosphite for flexible PU foam.<sup>195</sup> The treated foam self-extinguishes the flame during UL-94 tests in a vertical configuration. In addition, a conspicuous reduction in pkHRR (-60%) was observed in cone calorimetry (at a flux of 50 kW/m<sup>2</sup>). The same authors evaluated the FR mechanism behind the achieved results, revealing a condensed phase effect involving an intumescent layer, comprising SiO<sub>2</sub> and Si-O-P networks, as well as a gas phase effect related to the release of diethyl phosphite as a free radical scavenger.<sup>196</sup> Shi et al. exploited TEOS in combination with a polyacrylate resin in order to deposit a protective coating filled with silica nanoparticles on the surface of a melamine-formaldehyde foam. The presence of the coating further improved upon the already good FR properties of the uncoated foam, as demonstrated by an increase of the LOI (up to 43.7%).<sup>197</sup>

Recently, a sol-gel approach combined with freeze-drying has been employed to produce a silica aerogel to be exploited as either filler or surface coating for rigid PU foams.<sup>198</sup> When employed as a coating, the aerogel achieves the best FR properties, with LOI up to 29.4%, V0 classification by UL-94, and considerably reduced pkHRR values. Similar to open cell PU foam, the sol-gel approach has also been exploited to coat wood substrates.<sup>199</sup> An early study employed titanium(IV) isopropoxide on pine sapwood wood.<sup>200</sup> The treatment penetrated inside the wood structure, achieving different results based on the precursor concentration. Within this context, it is important to note how the possibility to perform a sol-gel process by mixing different solvent might reduce the surface tension of the sol and thus improve wettability. The impregnated wood displays improved char forming ability and an increase in LOI up to 38% (as well as a decrease in the pkHRR in cone calorimetry). The flammability, evaluated by UL-94 shows limited improvement with coated samples, achieving an HB classification while failing the test in a vertical configuration. Recently, Bellayer et al. reported a sol-gel formulation encompassing tetraethoxysilicate, methyltriethoxysilicate, 3-aminopropyl triethoxysilane, and diethyl phosphite that was either impregnated into the wood structure or deposited as thick coating.<sup>201</sup> The latter process was achieved by partially drying the solution in order to achieve a viscosity suitable for a doctor blade application. The adopted sol-gel formulation improved the FR properties of wood only when deposited as thick coating. The intumescent behavior of the coating also thermally insulated the underlying wood during a small-scale furnace test (Figure 14.5c).

#### 14.4.3 OUTLOOK AND FUTURE RESEARCH DIRECTIONS

The sol-gel approach has been clearly demonstrated as a viable tool for conferring flame retardant properties to different substrates. The ease of design and the versatility of the sol-gel chemistry is a key factor in the successful development of these kind of coatings in the FR field. The ability

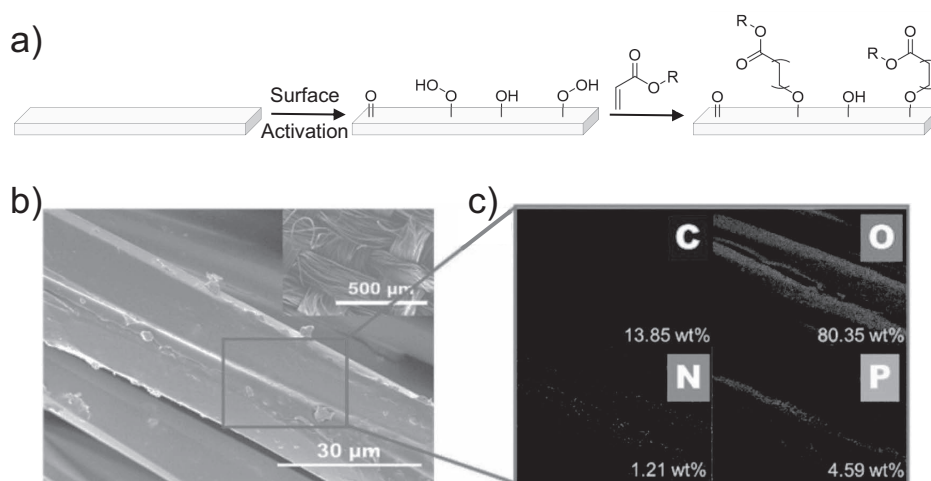
to tune the polarity of sol-gel precursors and the use of different solvents further allow adjusting the overall polarity of the sol based on the substrate choice. On the other hand, the need for additional solvents besides water might lead to waste management problems if large volumes are employed. Another drawback, mostly related to textiles, is represented by the durability of the coating to washing or abrasion. Although the use of different cross-linking strategies or the implementation of hydrophobic components might improve the wash-fastness of the coating, the literature shows that the FR efficiency of the coating is partially lost after few laundering cycles. A last problem to be addressed is related to scale-up. As discussed in the previous chapters, the best performing sol-gel solutions rely on the use of novel synthesized precursors that will require cost-effective production for commercial use.

### 14.5 PLASMA AND VAPOR BASED TREATMENTS

While layer-by-layer assembly, polyelectrolyte complexation, and sol-gel coatings represent the most active areas for flame retardant coating research, other approaches are worth noting in the context of this subfield. Of particular note are plasma- and vapor-based treatments, which make use of vapor deposition and/or plasma assisted polymerization to deposit or graft a flame retardant treatment to a substrate.<sup>2,202,203</sup> These approaches not only yield highly conformal coatings but also modify the surface of the substrate to covalently attach the polymerized monomers onto the surface. A chief advantage of this technique is the installation of the FR agent through a covalent bond. Covalent attachment generally yields treatments which are more durable to washing, which is especially important for textile finishes.

Plasma, the so-called fourth state of matter, is a quasi-neutral gas with a high degree of free ionic and radical species. Exposure of gaseous monomers to a plasma environment can lead to polymerization, yielding networked polymers of irregular topology due to the incidence of molecular rearrangement in the plasma environment.<sup>204</sup> The plasma can cause radical propagation in the gas state as well as on the surface of a material through adsorption and subsequent reaction of “activated” species. After decades of study, this once-challenging state of matter has been made significantly more available to researchers and industry through the advent of atmospheric plasmas.<sup>205,206</sup> The network-forming and surface-grafting tendencies of plasma polymerization are conceptually appealing because of the durability of networks to dissolution, which can impart wash resistance.

Plasma-driven polymerization for flame protection has been studied for many decades, with the earliest work polymerizing polysiloxanes onto the surface of polyacrylonitrile and polyamides.<sup>207–209</sup> The plasma process is especially amenable to utilizing mixed or sequential treatments of gases to deposit a coating. The modularity of the plasma treatment process has been used to deposit multifunctional



**FIGURE 14.6** (a) Schematic of the activation of surface functional groups from a plasma treatment, followed by the surface-initiated polymerization after exposure to a generic acrylate monomer. Most radically-polymerizable groups can be substituted for or incorporated with the acrylate shown. (b) Electron microscopy along with (c) energy dispersive spectroscopy (EDS) of phosphate-acrylate coated polyester fibers. The coating is clearly highly conformal to the fibers along with a uniform distribution of constituent elements along the fibers. Parts (b) and (c) reproduced from Ref. <sup>216</sup> with permission.

(typically flame retardant and hydrophobic) treatments through either the use of two monomers (e.g., a phosphonated acrylate and a fluorinated acrylate, see Figure 14.6a) or through sequential treatment by a flame retardant monomer followed by  $\text{SF}_6$  to add a water-repellant layer.<sup>210,211</sup> Plasma treatment has also been used historically to improve the adhesion of nanoparticles, such as clays or vapor-deposited carbon to textile fibers, that improve coating durability.<sup>212–214</sup> Recently, efforts have been made to afford the ability for plasma treatments for textile processing, offering hope for widespread adoption of these technologies.<sup>205</sup>

Plasma-assisted treatments have continued to be an active research area in recent years. An especially useful development has been the unique crosslinking network topologies. Recent work in plasma coatings has focused on multiplexing the capabilities of UV curing for rapid coating deposition along with plasma activation for covalent surface grafting by the photopolymerized species. This motif has led to wash-durable treatments for cotton and pure polyester fabric (Figure 14.6b,c).<sup>215,216</sup> Success in these research efforts could lead to more overlap between plasma treatments and other popular forms of flame retardant coating research (e.g., LbL, PEC, sol-gel, etc.) to improve durability. Plasma treatments have to this point focused primarily on textile treatment, owing to the volume of that market and the relative ease of implementation on commercially relevant scales. There have been promising results with plasma treatments on polyurethane foams,<sup>217</sup> but more work needs to be done to make this technology viable for commercial production.

An important advantage of plasma treatments, as compared to the other techniques discussed in this chapter, is that the gaseous nature of the polymerized species removes the need for any immersions of the substrate. By eliminating

solution immersion steps, coating processes can be faster and avoid time and energy intensive rinsing and drying steps. As plasma treatment technologies become cheaper and more widespread, they will continue to represent an important segment of FR-application technologies. Future research to develop multifunctional (e.g., antimicrobial/FR or hydrophobic/FR) treatments from the same monomer feedstock will further improve the utility of plasma treatments. Considerable work remains to be done for non-textile substrates. Foam and wood in particular could achieve significant improvements in fire safety, albeit while facing scaling issues owing to how plasmas are formed.

## 14.6 CONCLUSIONS

In this chapter we have described the most active current research areas in conformal flame retardant treatments: layer-by-layer assembly, polyelectrolyte complexation, sol-gel coatings, and plasma treatments. Layer-by-layer and polyelectrolyte complex treatments are the most active research areas in this subfield of fire protection currently, owing to their modularity, advantageous environmental profile, and high efficacy on a variety of substrates. Each of the described methodologies have significant hurdles to overcome prior to widespread commercialization and use. A chief concern for most of the described techniques is durability to laundering and weathering. Furthermore, the environmental ramifications of both the materials used and the process of deposition must be carefully considered if the global effort towards a circular economy is to be realized. Continued research and investment in these technologies promises to yield highly effective and environmentally benign fire protection for nearly any flammable material encountered in everyday life.



## REFERENCES

- (1) Little, R. W.; Church, J. M.; Coppick, S. Commercial Application of Flame-Resistant Finishes. *Industrial & Engineering Chemistry* **1950**, *42* (3), 432–440. <https://doi.org/10.1021/ie50483a015>.
- (2) Liu, B.; Zhao, H.; Wang, Y. Advanced Flame-Retardant Methods for Polymeric Materials. *Advanced Materials* **2022**, 2107905. <https://doi.org/10.1002/adma.202107905>.
- (3) Lazar, S. T.; Kolibaba, T. J.; Grunlan, J. C. Flame-Retardant Surface Treatments. *Nature Reviews Materials* **2020**, *5* (4), 259–275. <https://doi.org/10.1038/s41578-019-0164-6>.
- (4) Hoebel, J. F.; Damant, G. H.; Spivak, S. M.; Berlin, G. N. Clothing-Related Burn Casualties: An Overlooked Problem? *Fire Technology* **2010**, *46* (3), 629–649. <https://doi.org/10.1007/s10694-009-0113-9>.
- (5) Bourbigot, S.; Chlebicki, S.; Mamleev, V. Thermal Degradation of Cotton under Linear Heating. *Polymer Degradation and Stability* **2002**, *78* (1), 57–62. [https://doi.org/10.1016/S0141-3910\(02\)00119-2](https://doi.org/10.1016/S0141-3910(02)00119-2).
- (6) Kandola, B. K.; Horrocks, S.; Horrocks, A. R. Evidence of Interaction in Flame-Retardant Fibre-Intumescent Combinations by Thermal Analytical Techniques. *Thermochimica Acta* **1997**, *294* (1), 113–125. [https://doi.org/10.1016/S0040-6031\(96\)03151-6](https://doi.org/10.1016/S0040-6031(96)03151-6).
- (7) Buxbaum, L. H. The Degradation of Poly(Ethylene Terephthalate). *Angewandte Chemie International Edition in English* **1968**, *7* (3), 182–190. <https://doi.org/10.1002/anie.196801821>.
- (8) Holland, B. J.; Hay, J. N. Thermal Degradation of Nylon Polymers. *Polymer International* **2000**, *49* (9), 943–948. [https://doi.org/10.1002/1097-0126\(200009\)49:9<943::AID-PI400>3.0.CO;2-5](https://doi.org/10.1002/1097-0126(200009)49:9<943::AID-PI400>3.0.CO;2-5).
- (9) Hilado, C. J. An Overview of the Fire Behavior of Polymers. *Fire Technology* **1973**, *9* (3), 198–208. <https://doi.org/10.1007/BF02624777>.
- (10) Yang, C. Q.; He, Q. Textile Heat Release Properties Measured by Microscale Combustion Calorimetry: Experimental Repeatability. *Fire and Materials* **2012**, *36* (2), 127–137. <https://doi.org/10.1002/fam.1093>.
- (11) Lawton, E. L.; Setzer, C. J. Flame-Retardant Polyethylene Terephthalate Fibers. In *Flame-Retardant Polymeric Materials*; Lewin, M., Atlas, S. M., Pearce, E. M., Eds.; Springer: Boston, MA, 1975; pp 193–221. [https://doi.org/10.1007/978-1-4684-2148-4\\_4](https://doi.org/10.1007/978-1-4684-2148-4_4).
- (12) Hall, S.; Everts, B. *Fire Loss in the United States During 2021*; National Fire Protection Agency: Quincy, MA, 2022.
- (13) Dubrulle, L.; Zammarano, M.; Davis, R. D. *Effect of Fire-Retardant Coatings and Accelerated-Weathering on the Flammability of Wood-Based Materials in Wildland-Urban Interface (WUI) Communities*; National Institute of Standards and Technology, 2020. <https://doi.org/10.6028/NIST.TN.2094>.
- (14) Rutherford, D. W.; Wershaw, R. L.; Cox, L. G. *Changes in Composition and Porosity Occurring During the Thermal Degradation of Wood and Wood Components*; Scientific Investigations Report 2004–5292; United States Geological Survey: Reston, VA, 2005.
- (15) Hill, C. A. S. *Wood Modification: Chemical, Thermal and Other Processes*; John Wiley & Sons, Ltd: Chichester, UK, 2006. <https://doi.org/10.1002/0470021748>.
- (16) Lowden, L. A.; Hull, T. R. Flammability Behaviour of Wood and a Review of the Methods for Its Reduction. *Fire Science Reviews* **2013**, *2* (1), 4.
- (17) Liang, C.; Gracida-Alvarez, U. R.; Gallant, E. T.; Gillis, P. A.; Marques, Y. A.; Abramo, G. P.; Hawkins, T. R.; Dunn, J. B. Material Flows of Polyurethane in the United States. *Environmental Science & Technology* **2021**, *55* (20), 14215–14224. <https://doi.org/10.1021/acs.est.1c03654>.
- (18) Yadav, A.; de Souza, F. M.; Dawsey, T.; Gupta, R. K. Recent Advancements in Flame-Retardant Polyurethane Foams: A Review. *Industrial & Engineering Chemistry Research* **2022**, *61* (41), 15046–15065. <https://doi.org/10.1021/acs.iecr.2c02670>.
- (19) Iler, R. K. Multilayers of Colloidal Particles. *Journal of Colloid and Interface Science* **1966**, *21* (6), 569–594. [https://doi.org/10.1016/0095-8522\(66\)90018-3](https://doi.org/10.1016/0095-8522(66)90018-3).
- (20) Decher, G.; Hong, J.-D. Buildup of Ultrathin Multilayer Films by a Self-Assembly Process, I Consecutive Adsorption of Anionic and Cationic Bipolar Amphiphiles on Charged Surfaces. *Makromolekulare Chemie. Macromolecular Symposia* **1991**, *46* (1), 321–327. <https://doi.org/10.1002/masy.19910460145>.
- (21) Zhang, X.; Xu, Y.; Zhang, X.; Wu, H.; Shen, J.; Chen, R.; Xiong, Y.; Li, J.; Guo, S. Progress on the Layer-by-Layer Assembly of Multilayered Polymer Composites: Strategy, Structural Control and Applications. *Progress in Polymer Science* **2019**, *89*, 76–107. <https://doi.org/10.1016/j.progpolymsci.2018.10.002>.
- (22) Decher, G.; Schlenoff, J. B. *Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials*, 2nd ed.; John Wiley & Sons, Ltd.: Weinheim, Germany, **2012**.
- (23) Yang, H.; Yu, B.; Song, P.; Maluk, C.; Wang, H. Surface-Coating Engineering for Flame Retardant Flexible Polyurethane Foams: A Critical Review. *Composites Part B: Engineering* **2019**, *176*, 107185. <https://doi.org/10.1016/j.compositesb.2019.107185>.
- (24) Qiu, X.; Li, Z.; Li, X.; Zhang, Z. Flame Retardant Coatings Prepared Using Layer by Layer Assembly: A Review. *Chemical Engineering Journal* **2018**, *334*, 108–122. <https://doi.org/10.1016/j.cej.2017.09.194>.
- (25) Liang, S.; Neisius, N. M.; Gaan, S. Recent Developments in Flame Retardant Polymeric Coatings. *Progress in Organic Coatings* **2013**, *76* (11), 1642–1665. <https://doi.org/10.1016/j.porgcoat.2013.07.014>.
- (26) Kundu, C. K.; Li, Z.; Song, L.; Hu, Y. An Overview of Fire Retardant Treatments for Synthetic Textiles: From Traditional Approaches to Recent Applications. *European Polymer Journal* **2020**, *137*, 109911. <https://doi.org/10.1016/j.eurpolymj.2020.109911>.
- (27) Ariga, K.; Ahn, E.; Park, M.; Kim, B. Layer-by-Layer Assembly: Recent Progress from Layered Assemblies to Layered Nanoarchitectonics. *Chemistry: An Asian Journal* **2019**, *14* (15), 2553–2566. <https://doi.org/10.1002/asia.201900627>.
- (28) van der Gucht, J.; Spruijt, E.; Lemmers, M.; Cohen Stuart, M. A. Polyelectrolyte Complexes: Bulk Phases and Colloidal Systems. *Journal of Colloid and Interface Science* **2011**, *361* (2), 407–422. <https://doi.org/10.1016/j.jcis.2011.05.080>.
- (29) Gilman, J. W.; Harris, R. H.; Shields, J. R.; Kashiwagi, T.; Morgan, A. B. A Study of the Flammability Reduction Mechanism of Polystyrene-Layered Silicate Nanocomposite: Layered Silicate Reinforced Carbonaceous Char. *Polymers for Advanced Technologies* **2006**, *17* (4), 263–271. <https://doi.org/10.1002/pat.682>.
- (30) Gilman, J. W.; Jackson, C. L.; Morgan, A. B.; Harris, R.; Manias, E.; Giannelis, E. P.; Wuthenow, M.; Hilton, D.; Phillips, S. H. Flammability Properties of Polymer-Layered-Silicate Nanocomposites. Polypropylene and Polystyrene Nanocomposites. *Chemistry of Materials* **2000**, *12* (7), 1866–1873. <https://doi.org/10.1021/cm0001760>.

- (31) Schartel, B.; Bartholmai, M.; Knoll, U. Some Comments on the Main Fire Retardancy Mechanisms in Polymer Nanocomposites. *Polymers for Advanced Technologies* **2006**, *17* (9–10), 772–777. <https://doi.org/10.1002/pat.792>.
- (32) Alongi, J.; Han, Z.; Bourbigot, S. Intumescence: Tradition versus Novelty. A Comprehensive Review. *Progress in Polymer Science* **2015**, *51*, 28–73. <https://doi.org/10.1016/j.progpolymsci.2015.04.010>.
- (33) Zhang, L.; Li, Y.; Sun, J.; Shen, J. Mechanically Stable Antireflection and Antifogging Coatings Fabricated by the Layer-by-Layer Deposition Process and Postcalcination. *Langmuir* **2008**, *24* (19), 10851–10857. <https://doi.org/10.1021/la801806r>.
- (34) Li, Y.; Liu, F.; Sun, J. A Facile Layer-by-Layer Deposition Process for the Fabrication of Highly Transparent Superhydrophobic Coatings. *Chemical Communications* **2009**, *19*, 2730. <https://doi.org/10.1039/b900804g>.
- (35) Li, P.; Wang, B.; Xu, Y.-J.; Jiang, Z.; Dong, C.; Liu, Y.; Zhu, P. Ecofriendly Flame-Retardant Cotton Fabrics: Preparation, Flame Retardancy, Thermal Degradation Properties, and Mechanism. *ACS Sustainable Chemistry & Engineering* **2019**, *7* (23), 19246–19256. <https://doi.org/10.1021/acssuschemeng.9b05523>.
- (36) Chen, X.; Fang, F.; Zhang, X.; Ding, X.; Wang, Y.; Chen, L.; Tian, X. Flame-Retardant, Electrically Conductive and Antimicrobial Multifunctional Coating on Cotton Fabric via Layer-by-Layer Assembly Technique. *RSC Advances* **2016**, *6* (33), 27669–27676. <https://doi.org/10.1039/C5RA26914H>.
- (37) Ahmed, H. B.; Emam, H. E. Layer by Layer Assembly of Nanosilver for High Performance Cotton Fabrics. *Fibers and Polymers* **2016**, *17* (3), 418–426. <https://doi.org/10.1007/s12221-016-5814-3>.
- (38) Uğur, Ş. S. Sustainable Dyeing and Finishing of Cotton Fabrics with Layer-by-Layer Technique. *Coatings* **2023**, *13* (6), 1129. <https://doi.org/10.3390/coatings13061129>.
- (39) Izquierdo, A.; Ono, S. S.; Voegel, J.-C.; Schaaf, P.; Decher, G. Dipping versus Spraying: Exploring the Deposition Conditions for Speeding Up Layer-by-Layer Assembly. *Langmuir* **2005**, *21* (16), 7558–7567. <https://doi.org/10.1021/la047407s>.
- (40) Dierendonck, M.; De Koker, S.; De Rycke, R.; De Geest, B. G. Just Spray It—LbL Assembly Enters a New Age. *Soft Matter* **2014**, *10* (6), 804–807. <https://doi.org/10.1039/C3SM52202D>.
- (41) Alongi, J.; Carosio, F.; Frache, A.; Malucelli, G. Layer by Layer Coatings Assembled through Dipping, Vertical or Horizontal Spray for Cotton Flame Retardancy. *Carbohydrate Polymers* **2013**, *92* (1), 114–119. <https://doi.org/10.1016/j.carbpol.2012.08.086>.
- (42) Alongi, J.; Malucelli, G. Cotton Flame Retardancy: State of the Art and Future Perspectives. *RSC Advances* **2015**, *5* (31), 24239–24263. <https://doi.org/10.1039/C5RA01176K>.
- (43) Zhao, H.-B.; Wang, Y.-Z. Design and Synthesis of PET-Based Copolyesters with Flame-Retardant and Antidripping Performance. *Macromolecular Rapid Communications* **2017**, *38* (23), 1700451. <https://doi.org/10.1002/marc.201700451>.
- (44) Guin, T.; Kreckler, M.; Milhorn, A.; Grunlan, J. C. Maintaining Hand and Improving Fire Resistance of Cotton Fabric through Ultrasonication Rinsing of Multilayer Nanocoating. *Cellulose* **2014**, *21* (4), 3023–3030. <https://doi.org/10.1007/s10570-014-0286-3>.
- (45) Alongi, J.; Carosio, F.; Malucelli, G. Influence of Ammonium Polyphosphate-/Poly(Acrylic Acid)-Based Layer by Layer Architectures on the Char Formation in Cotton, Polyester and Their Blends. *Polymer Degradation and Stability* **2012**, *97* (9), 1644–1653. <https://doi.org/10.1016/j.polymdegradstab.2012.06.025>.
- (46) Li, Y.-C.; Mannen, S.; Morgan, A. B.; Chang, S.; Yang, Y.-H.; Condon, B.; Grunlan, J. C. Intumescent All-Polymer Multilayer Nanocoating Capable of Extinguishing Flame on Fabric. *Advanced Materials* **2011**, *23* (34), 3926–3931. <https://doi.org/10.1002/adma.201101871>.
- (47) Carosio, F.; Fontaine, G.; Alongi, J.; Bourbigot, S. Starch-Based Layer by Layer Assembly: Efficient and Sustainable Approach to Cotton Fire Protection. *ACS Applied Materials & Interfaces* **2015**, *7* (22), 12158–12167. <https://doi.org/10.1021/acsami.5b02507>.
- (48) Zhang, T.; Yan, H.; Wang, L.; Fang, Z. Controlled Formation of Self-Extinguishing Intumescent Coating on Ramie Fabric via Layer-by-Layer Assembly. *Industrial & Engineering Chemistry Research* **2013**, *52* (18), 6138–6146. <https://doi.org/10.1021/ie3031554>.
- (49) Carosio, F.; Alongi, J. Few Durable Layers Suppress Cotton Combustion Due to the Joint Combination of Layer by Layer Assembly and UV-Curing. *RSC Advances* **2015**, *5* (87), 71482–71490. <https://doi.org/10.1039/C5RA11856E>.
- (50) Apaydin, K.; Laachachi, A.; Ball, V.; Jimenez, M.; Bourbigot, S.; Toniazio, V.; Ruch, D. Intumescent Coating of (Polyallylamine-Polyphosphates) Deposited on Polyamide Fabrics via Layer-by-Layer Technique. *Polymer Degradation and Stability* **2014**, *106*, 158–164. <https://doi.org/10.1016/j.polymdegradstab.2014.01.006>.
- (51) Zhao, L.; Yan, H.; Fang, Z.; Wang, J.; Wang, H. On the Flameproof Treatment of Ramie Fabrics Using a Spray-Assisted Layer-by-Layer Technique. *Polymer Degradation and Stability* **2015**, *121*, 11–17. <https://doi.org/10.1016/j.polymdegradstab.2015.08.007>.
- (52) Fu, C.; Xu, X.; Yin, G.-Z.; Xu, B.; Li, P.; Ai, B.; Zhai, Z.; Gao, F.; Zhai, J.; Wang, D.-Y. Surface Engineering for Cellulose as a Boosted Layer-by-Layer Assembly: Excellent Flame Retardancy and Improved Durability with Introduction of Bio-Based “Molecular Glue.” *Applied Surface Science* **2022**, *585*, 152550. <https://doi.org/10.1016/j.apsusc.2022.152550>.
- (53) Carosio, F.; Di Blasio, A.; Alongi, J.; Malucelli, G. Green DNA-Based Flame Retardant Coatings Assembled through Layer by Layer. *Polymer* **2013**, *54* (19), 5148–5153. <https://doi.org/10.1016/j.polymer.2013.07.029>.
- (54) Zhang, W.; Wang, M.; Guan, J.-P.; Tang, R.-C.; Qiao, Y.-F. Casein Phosphopeptide-Metal Salts Combination: A Novel Route for Imparting the Durable Flame Retardancy to Silk. *Journal of the Taiwan Institute of Chemical Engineers* **2019**, *101*, 1–7. <https://doi.org/10.1016/j.jtice.2019.04.038>.
- (55) Lv, Z.; Hu, Y.-T.; Guan, J.-P.; Tang, R.-C.; Chen, G.-Q. Preparation of a Flame Retardant, Antibacterial, and Colored Silk Fabric with Chitosan and Vitamin B2 Sodium Phosphate by Electrostatic Layer by Layer Assembly. *Materials Letters* **2019**, *241*, 136–139. <https://doi.org/10.1016/j.matlet.2019.01.005>.
- (56) Mokhena, T. C.; Sadiku, E. R.; Ray, S. S.; Mochane, M. J.; Matabola, K. P.; Motloung, M. Flame Retardancy Efficacy of Phytic Acid: An Overview. *Journal of Applied Polymer Science* **2022**, *139* (27). <https://doi.org/10.1002/app.52495>.
- (57) Magovac, E.; Jordanov, I.; Grunlan, J. C.; Bischof, S. Environmentally-Benign Phytic Acid-Based Multilayer Coating for Flame Retardant Cotton. *Materials* **2020**, *13* (23), 5492. <https://doi.org/10.3390/ma13235492>.
- (58) Liu, L.; Huang, Z.; Pan, Y.; Wang, X.; Song, L.; Hu, Y. Finishing of Cotton Fabrics by Multi-Layered Coatings to

- Improve Their Flame Retardancy and Water Repellency. *Cellulose* **2018**, *25* (8), 4791–4803. <https://doi.org/10.1007/s10570-018-1866-4>.
- (59) Li, Y.-C.; Schulz, J.; Mannen, S.; Delhom, C.; Condon, B.; Chang, S.; Zammarano, M.; Grunlan, J. C. Flame Retardant Behavior of Polyelectrolyte–Clay Thin Film Assemblies on Cotton Fabric. *ACS Nano* **2010**, *4* (6), 3325–3337. <https://doi.org/10.1021/nn100467e>.
- (60) Laufer, G.; Carosio, F.; Martinez, R.; Camino, G.; Grunlan, J. C. Growth and Fire Resistance of Colloidal Silica-Polyelectrolyte Thin Film Assemblies. *Journal of Colloid and Interface Science* **2011**, *356* (1), 69–77. <https://doi.org/10.1016/j.jcis.2010.12.072>.
- (61) Wang, D.; Ma, J.; Liu, J.; Tian, A.; Fu, S. Intumescent Flame-retardant and Ultraviolet-blocking Coating Screen-Printed on Cotton Fabric. *Cellulose* **2021**, *28* (4), 2495–2504. <https://doi.org/10.1007/s10570-020-03669-7>.
- (62) Zhang, Y.; Tian, W.; Liu, L.; Cheng, W.; Wang, W.; Liew, K. M.; Wang, B.; Hu, Y. Eco-Friendly Flame Retardant and Electromagnetic Interference Shielding Cotton Fabrics with Multi-Layered Coatings. *Chemical Engineering Journal* **2019**, *372*, 1077–1090. <https://doi.org/10.1016/j.cej.2019.05.012>.
- (63) Carosio, F.; Di Pierro, A.; Alongi, J.; Fina, A.; Saracco, G. 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. *Journal of Colloid and Interface Science* **2018**, *510*, 142–151. <https://doi.org/10.1016/j.jcis.2017.09.059>.
- (64) Carosio, F.; Laufer, G.; Alongi, J.; Camino, G.; Grunlan, J. C. Layer-by-Layer Assembly of Silica-Based Flame Retardant Thin Film on PET Fabric. *Polymer Degradation and Stability* **2011**, *96* (5), 745–750. <https://doi.org/10.1016/j.polymdegradstab.2011.02.019>.
- (65) Carosio, F.; Di Blasio, A.; Cuttica, F.; Alongi, J.; Frache, A.; Malucelli, G. Flame Retardancy of Polyester Fabrics Treated by Spray-Assisted Layer-by-Layer Silica Architectures. *Industrial & Engineering Chemistry Research* **2013**, *52* (28), 9544–9550. <https://doi.org/10.1021/ie4011244>.
- (66) Liu, J.; Xiao, C. Fire-Retardant Multilayer Assembled on Polyester Fabric from Water-Soluble Chitosan, Sodium Alginate and Divalent Metal Ion. *International Journal of Biological Macromolecules* **2018**, *119*, 1083–1089. <https://doi.org/10.1016/j.ijbiomac.2018.08.043>.
- (67) Pan, Y.; Liu, L.; Song, L.; Hu, Y.; Wang, W.; Zhao, H. Durable Flame Retardant Treatment of Polyethylene Terephthalate (PET) Fabric with Cross-Linked Layer-by-Layer Assembled Coating. *Polymer Degradation and Stability* **2019**, *165*, 145–152. <https://doi.org/10.1016/j.polymdegradstab.2019.05.009>.
- (68) Fang, Y.; Liu, X.; Tao, X. Intumescent Flame Retardant and Anti-Dripping of PET Fabrics through Layer-by-Layer Assembly of Chitosan and Ammonium Polyphosphate. *Progress in Organic Coatings* **2019**, *134*, 162–168. <https://doi.org/10.1016/j.porgcoat.2019.05.010>.
- (69) Jordanov, I.; Magovac, E.; Fahami, A.; Lazar, S.; Kolibaba, T.; Smith, R. J.; Bischof, S.; Grunlan, J. C. Flame Retardant Polyester Fabric from Nitrogen-Rich Low Molecular Weight Additives within Intumescent Nanocoating. *Polymer Degradation and Stability* **2019**, *170*, 108998. <https://doi.org/10.1016/j.polymdegradstab.2019.108998>.
- (70) Guo, J.; Cang, D.; Zhao, Z.; Yin, Y.; Yang, Z.; Saiyin, B. Fabrication of Superhydrophobic and Flame-Retardant Polyethylene Terephthalate Fabric through a Fluorine-Free Layer-by-Layer Technique. *International Journal of Chemical Reactor Engineering* **2022**, *20* (12), 1283–1295. <https://doi.org/10.1515/ijcre-2022-0010>.
- (71) Kumar Kundu, C.; Wang, W.; Zhou, S.; Wang, X.; Sheng, H.; Pan, Y.; Song, L.; Hu, Y. A Green Approach to Constructing Multilayered Nanocoating for Flame Retardant Treatment of Polyamide 66 Fabric from Chitosan and Sodium Alginate. *Carbohydrate Polymers* **2017**, *166*, 131–138. <https://doi.org/10.1016/j.carbpol.2017.02.084>.
- (72) Kundu, C. K.; Wang, X.; Song, L.; Hu, Y. Borate Cross-Linked Layer-by-Layer Assembly of Green Polyelectrolytes on Polyamide 66 Fabrics for Flame-Retardant Treatment. *Progress in Organic Coatings* **2018**, *121*, 173–181. <https://doi.org/10.1016/j.porgcoat.2018.04.031>.
- (73) Yoon, H. N.; Buckley, A. Improved Comfort Polyester: Part I: Transport Properties and Thermal Comfort of Polyester/Cotton Blend Fabrics. *Textile Research Journal* **1984**, *54* (5), 289–298. <https://doi.org/10.1177/004051758405400502>.
- (74) Alongi, J.; Carosio, F.; Kiekens, P. Recent Advances in the Design of Water Based-Flame Retardant Coatings for Polyester and Polyester-Cotton Blends. *Polymers* **2016**, *8* (10), 357. <https://doi.org/10.3390/polym8100357>.
- (75) Fang, Y.; Sun, W.; Li, J.; Liu, H.; Liu, X. Eco-Friendly Flame Retardant and Dripping-Resistant of Polyester/Cotton Blend Fabrics through Layer-by-Layer Assembly Fully Bio-Based Chitosan/Phytic Acid Coating. *International Journal of Biological Macromolecules* **2021**, *175*, 140–146. <https://doi.org/10.1016/j.ijbiomac.2021.02.023>.
- (76) Wang, B.; Xu, Y.-J.; Li, P.; Zhang, F.-Q.; Liu, Y.; Zhu, P. Flame-Retardant Polyester/Cotton Blend with Phosphorus/Nitrogen/Silicon-Containing Nano-Coating by Layer-by-Layer Assembly. *Applied Surface Science* **2020**, *509*, 145323. <https://doi.org/10.1016/j.apsusc.2020.145323>.
- (77) Narkhede, M.; Thota, S.; Mosurkal, R.; Muller, W. S.; Kumar, J. Layer-by-Layer Assembly of Halogen-Free Polymeric Materials on Nylon/Cotton Blend for Flame Retardant Applications: Layer-by-Layer Assembly of Halogen-Free Polymeric Materials. *Fire and Materials* **2016**, *40* (2), 206–218. <https://doi.org/10.1002/fam.2280>.
- (78) Smith, D. L.; Vest, N. A.; Rodriguez-Melendez, D.; Palen, B.; Grunlan, J. C. Bio-Sourced Intumescent Nanocoating. *Advanced Engineering Materials* **2023**, *25* (4), 2200911. <https://doi.org/10.1002/adem.202200911>.
- (79) Carosio, F.; Alongi, J. Influence of Layer by Layer Coatings Containing Octapropylammonium Polyhedral Oligomeric Silsesquioxane and Ammonium Polyphosphate on the Thermal Stability and Flammability of Acrylic Fabrics. *Journal of Analytical and Applied Pyrolysis* **2016**, *119*, 114–123. <https://doi.org/10.1016/j.jaap.2016.03.010>.
- (80) Ren, Y.; Huo, T.; Qin, Y.; Liu, X. Preparation of Flame Retardant Polyacrylonitrile Fabric Based on Sol-Gel and Layer-by-Layer Assembly. *Materials* **2018**, *11* (4), 483. <https://doi.org/10.3390/ma11040483>.
- (81) Kim, Y. S.; Davis, R.; Cain, A. A.; Grunlan, J. C. Development of Layer-by-Layer Assembled Carbon Nanofiber-Filled Coatings to Reduce Polyurethane Foam Flammability. *Polymer* **2011**, *52* (13), 2847–2855. <https://doi.org/10.1016/j.polymer.2011.04.023>.
- (82) Liu, Q.; Gao, S.; Zhao, Y.; Tao, W.; Yu, X.; Zhi, M. Review of Layer-by-Layer Self-Assembly Technology for Fire Protection of Flexible Polyurethane Foam. *Journal of Materials Science* **2021**, *56* (16), 9605–9643. <https://doi.org/10.1007/s10853-021-05904-3>.
- (83) Carosio, F.; Ghanadpour, M.; Alongi, J.; Wågberg, L. Layer-by-Layer-Assembled Chitosan/Phosphorylated Cellulose

- Nanofibrils as a Bio-Based and Flame Protecting Nano-Exoskeleton on PU Foams. *Carbohydrate Polymers* **2018**, *202*, 479–487. <https://doi.org/10.1016/j.carbpol.2018.09.005>.
- (84) Krämer, R. H.; Zammarano, M.; Linteris, G. T.; Gedde, U. W.; Gilman, J. W. Heat Release and Structural Collapse of Flexible Polyurethane Foam. *Polymer Degradation and Stability* **2010**, *95* (6), 1115–1122. <https://doi.org/10.1016/j.polymdegradstab.2010.02.019>.
- (85) Haile, M.; Fomete, S.; Lopez, I. D.; Grunlan, J. C. Aluminum Hydroxide Multilayer Assembly Capable of Extinguishing Flame on Polyurethane Foam. *Journal of Materials Science* **2016**, *51* (1), 375–381. <https://doi.org/10.1007/s10853-015-9258-8>.
- (86) Pan, Y.; Zhan, J.; Pan, H.; Wang, W.; Ge, H.; Song, L.; Hu, Y. A Novel and Effective Method to Fabricate Flame Retardant and Smoke Suppressed Flexible Polyurethane Foam. *RSC Advances* **2015**, *5* (83), 67878–67885. <https://doi.org/10.1039/C5RA09553K>.
- (87) Lazar, S.; Shen, R.; Quan, Y.; Palen, B.; Wang, Q.; Ellison, C. J.; Grunlan, J. C. Mixed Solvent Synthesis of Polydopamine Nanospheres for Sustainable Multilayer Flame Retardant Nanocoating. *Polymer Chemistry* **2021**, *12* (16), 2389–2396. <https://doi.org/10.1039/D1PY00111F>.
- (88) Pan, Y.; Liu, L.; Cai, W.; Hu, Y.; Jiang, S.; Zhao, H. Effect of Layer-by-Layer Self-Assembled Sepiolite-Based Nanocoating on Flame Retardant and Smoke Suppressant Properties of Flexible Polyurethane Foam. *Applied Clay Science* **2019**, *168*, 230–236. <https://doi.org/10.1016/j.clay.2018.11.014>.
- (89) Pan, H.; Wang, W.; Pan, Y.; Song, L.; Hu, Y.; Liew, K. M. Formation of Layer-by-Layer Assembled Titanate Nanotubes Filled Coating on Flexible Polyurethane Foam with Improved Flame Retardant and Smoke Suppression Properties. *ACS Applied Materials & Interfaces* **2015**, *7* (1), 101–111. <https://doi.org/10.1021/am507045g>.
- (90) Smith, R. J.; Holder, K. M.; Ruiz, S.; Hahn, W.; Song, Y.; Lvov, Y. M.; Grunlan, J. C. Environmentally Benign Halloysite Nanotube Multilayer Assembly Significantly Reduces Polyurethane Flammability. *Advanced Functional Materials* **2018**, *28* (27), 1703289. <https://doi.org/10.1002/adfm.201703289>.
- (91) Holder, K. M.; Cain, A. A.; Plummer, M. G.; Stevens, B. E.; Odenborg, P. K.; Morgan, A. B.; Grunlan, J. C. Carbon Nanotube Multilayer Nanocoatings Prevent Flame Spread on Flexible Polyurethane Foam. *Macromolecular Materials and Engineering* **2016**, *301* (6), 665–673. <https://doi.org/10.1002/mame.201500327>.
- (92) Kim, Y. S.; Davis, R. Multi-Walled Carbon Nanotube Layer-by-Layer Coatings with a Trilayer Structure to Reduce Foam Flammability. *Thin Solid Films* **2014**, *550*, 184–189. <https://doi.org/10.1016/j.tsf.2013.10.167>.
- (93) Zhang, L.; Liu, B.-W.; Wang, Y.-Z.; Fu, T.; Zhao, H.-B. P-Doped PANI/AgMWs Nano/Micro Coating towards High-Efficiency Flame Retardancy and Electromagnetic Interference Shielding. *Composites Part B: Engineering* **2022**, *238*, 109944. <https://doi.org/10.1016/j.compositesb.2022.109944>.
- (94) Carosio, F.; Kochumalayil, J.; Cuttica, F.; Camino, G.; Berglund, L. Oriented Clay Nanopaper from Biobased Components—Mechanisms for Superior Fire Protection Properties. *ACS Applied Materials & Interfaces* **2015**, *7* (10), 5847–5856. <https://doi.org/10.1021/am509058h>.
- (95) Laufer, G.; Kirkland, C.; Cain, A. A.; Grunlan, J. C. Clay–Chitosan Nanobrick Walls: Completely Renewable Gas Barrier and Flame-Retardant Nanocoatings. *ACS Applied Materials & Interfaces* **2012**, *4* (3), 1643–1649. <https://doi.org/10.1021/am2017915>.
- (96) Kim, Y. S.; Li, Y.-C.; Pitts, W. M.; Werrel, M.; Davis, R. D. Rapid Growing Clay Coatings to Reduce the Fire Threat of Furniture. *ACS Applied Materials & Interfaces* **2014**, *6* (3), 2146–2152. <https://doi.org/10.1021/am405259n>.
- (97) Cain, A. A.; Plummer, M. G. B.; Murray, S. E.; Bolling, L.; Regev, O.; Grunlan, J. C. Iron-Containing, High Aspect Ratio Clay as Nanoarmor That Imparts Substantial Thermal/Flame Protection to Polyurethane with a Single Electrostatically-Deposited Bilayer. *Journal of Materials Chemistry A* **2014**, *2* (41), 17609–17617. <https://doi.org/10.1039/C4TA03541K>.
- (98) Lazar, S.; Carosio, F.; Davesne, A.-L.; Jimenez, M.; Bourbigot, S.; Grunlan, J. Extreme Heat Shielding of Clay/Chitosan Nanobrick Wall on Flexible Foam. *ACS Applied Materials & Interfaces* **2018**, *10* (37), 31686–31696. <https://doi.org/10.1021/acsami.8b10227>.
- (99) Maddalena, L.; Gomez, J.; Fina, A.; Carosio, F. Effects of Graphite Oxide Nanoparticle Size on the Functional Properties of Layer-by-Layer Coated Flexible Foams. *Nanomaterials* **2021**, *11* (2), 266. <https://doi.org/10.3390/nano11020266>.
- (100) Pan, H.; Yu, B.; Wang, W.; Pan, Y.; Song, L.; Hu, Y. 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 Advances* **2016**, *6* (115), 114304–114312. <https://doi.org/10.1039/C6RA15522G>.
- (101) Maddalena, L.; Carosio, F.; Gomez, J.; Saracco, G.; Fina, A. Layer-by-Layer Assembly of Efficient Flame Retardant Coatings Based on High Aspect Ratio Graphene Oxide and Chitosan Capable of Preventing Ignition of PU Foam. *Polymer Degradation and Stability* **2018**, *152*, 1–9. <https://doi.org/10.1016/j.polymdegradstab.2018.03.013>.
- (102) Carosio, F.; Maddalena, L.; Gomez, J.; Saracco, G.; Fina, A. Graphene Oxide Exoskeleton to Produce Self-Extinguishing, Nonignitable, and Flame Resistant Flexible Foams: A Mechanically Tough Alternative to Inorganic Aerogels. *Advanced Materials Interfaces* **2018**, *5* (23), 1801288. <https://doi.org/10.1002/admi.201801288>.
- (103) Lin, B.; Yuen, A. C. Y.; Li, A.; Zhang, Y.; Chen, T. B. Y.; Yu, B.; Lee, E. W. M.; Peng, S.; Yang, W.; Lu, H.-D.; Chan, Q. N.; Yeoh, G. H.; Wang, C. H. MXene/Chitosan Nanocoating for Flexible Polyurethane Foam towards Remarkable Fire Hazards Reductions. *Journal of Hazardous Materials* **2020**, *381*, 120952. <https://doi.org/10.1016/j.jhazmat.2019.120952>.
- (104) Lin, B.; Yuen, A. C. Y.; Oliver, S.; Liu, J.; Yu, B.; Yang, W.; Wu, S.; Yeoh, G. H.; Wang, C. H. Dual Functionalisation of Polyurethane Foam for Unprecedented Flame Retardancy and Antibacterial Properties Using Layer-by-Layer Assembly of MXene Chitosan with Antibacterial Metal Particles. *Composites Part B: Engineering* **2022**, *244*, 110147. <https://doi.org/10.1016/j.compositesb.2022.110147>.
- (105) Lin, B.; Yuen, A. C. Y.; Chen, T. B. Y.; Yu, B.; Yang, W.; Zhang, J.; Yao, Y.; Wu, S.; Wang, C. H.; Yeoh, G. H. Experimental and Numerical Perspective on the Fire Performance of MXene/Chitosan/Phytic Acid Coated Flexible Polyurethane Foam. *Scientific Reports* **2021**, *11* (1), 4684. <https://doi.org/10.1038/s41598-021-84083-2>.
- (106) Wang, X.; Pan, Y.-T.; Wan, J.-T.; Wang, D.-Y. An Eco-Friendly Way to Fire Retardant Flexible Polyurethane Foam: Layer-by-Layer Assembly of Fully Bio-Based

- Substances. *RSC Advances* **2014**, *4* (86), 46164–46169. <https://doi.org/10.1039/C4RA07972H>.
- (107) Pan, Y.; Zhan, J.; Pan, H.; Wang, W.; Tang, G.; Song, L.; Hu, Y. 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 Sustainable Chemistry & Engineering* **2016**, *4* (3), 1431–1438. <https://doi.org/10.1021/acsschemeng.5b01423>.
- (108) Laufer, G.; Kirkland, C.; Morgan, A. B.; Grunlan, J. C. Exceptionally Flame Retardant Sulfur-Based Multilayer Nanocoating for Polyurethane Prepared from Aqueous Polyelectrolyte Solutions. *ACS Macro Letters* **2013**, *2* (5), 361–365. <https://doi.org/10.1021/mz400105e>.
- (109) Carosio, F.; Di Blasio, A.; Cuttica, F.; Alongi, J.; Malucelli, G. Self-Assembled Hybrid Nanoarchitectures Deposited on Poly(Urethane) Foams Capable of Chemically Adapting to Extreme Heat. *RSC Advances* **2014**, *4* (32), 16674–16680. <https://doi.org/10.1039/C4RA01343C>.
- (110) Cain, A. A.; Nolen, C. R.; Li, Y.-C.; Davis, R.; Grunlan, J. C. Phosphorous-Filled Nanobrick Wall Multilayer Thin Film Eliminates Polyurethane Melt Dripping and Reduces Heat Release Associated with Fire. *Polymer Degradation and Stability* **2013**, *98* (12), 2645–2652. <https://doi.org/10.1016/j.polymdegradstab.2013.09.028>.
- (111) Weldemhret, T. G.; Menge, H. G.; Lee, D.-W.; Park, H.; Lee, J.; Song, J. I.; Park, Y. T. Facile Deposition of Environmentally Benign Organic-Inorganic Flame Retardant Coatings to Protect Flammable Foam. *Progress in Organic Coatings* **2021**, *161*, 106480. <https://doi.org/10.1016/j.porgcoat.2021.106480>.
- (112) Li, Y.-C.; Kim, Y. S.; Shields, J.; Davis, R. Controlling Polyurethane Foam Flammability and Mechanical Behaviour by Tailoring the Composition of Clay-Based Multilayer Nanocoatings. *Journal of Materials Chemistry A* **2013**, *1* (41), 12987. <https://doi.org/10.1039/c3ta11936j>.
- (113) Carosio, F.; Fina, A. Three Organic/Inorganic Nanolayers on Flexible Foam Allow Retaining Superior Flame Retardancy Performance Upon Mechanical Compression Cycles. *Frontiers in Materials* **2019**, *6*. <https://doi.org/10.3389/fmats.2019.00020>.
- (114) Song, Y.; Meyers, K. P.; Gerringer, J.; Ramakrishnan, R. K.; Humood, M.; Qin, S.; Polycarpou, A. A.; Nazarenko, S.; Grunlan, J. C. Fast Self-Healing of Polyelectrolyte Multilayer Nanocoating and Restoration of Super Oxygen Barrier. *Macromolecular Rapid Communications* **2017**, *38* (10), 1700064. <https://doi.org/10.1002/marc.201700064>.
- (115) Yang, J.-C.; Cao, Z.-J.; Wang, Y.-Z.; Schiraldi, D. A. Ammonium Polyphosphate-Based Nanocoating for Melamine Foam towards High Flame Retardancy and Anti-Shrinkage in Fire. *Polymer* **2015**, *66*, 86–93. <https://doi.org/10.1016/j.polymer.2015.04.022>.
- (116) Deng, S.-B.; Liao, W.; Yang, J.-C.; Cao, Z.-J.; Wang, Y.-Z. Flame-Retardant and Smoke-Suppressed Silicone Foams with Chitosan-Based Nanocoatings. *Industrial & Engineering Chemistry Research* **2016**, *55* (27), 7239–7248. <https://doi.org/10.1021/acs.iecr.6b00532>.
- (117) Carosio, F.; Cuttica, F.; Di Blasio, A.; Alongi, J.; Malucelli, G. Layer by Layer Assembly of Flame Retardant Thin Films on Closed Cell PET Foams: Efficiency of Ammonium Polyphosphate versus DNA. *Polymer Degradation and Stability* **2015**, *113*, 189–196. <https://doi.org/10.1016/j.polymdegradstab.2014.09.018>.
- (118) Köklükaya, O.; Carosio, F.; Grunlan, J. C.; Wågberg, L. Flame-Retardant Paper from Wood Fibers Functionalized via Layer-by-Layer Assembly. *ACS Applied Materials & Interfaces* **2015**, *7* (42), 23750–23759. <https://doi.org/10.1021/acsami.5b08105>.
- (119) Köklükaya, O.; Carosio, F.; Durán, V. L.; Wågberg, L. Layer-by-Layer Modified Low Density Cellulose Fiber Networks: A Sustainable and Fireproof Alternative to Petroleum Based Foams. *Carbohydrate Polymers* **2020**, *230*, 115616. <https://doi.org/10.1016/j.carbpol.2019.115616>.
- (120) Köklükaya, O.; Carosio, F.; Wågberg, L. Superior Flame-Resistant Cellulose Nanofibril Aerogels Modified with Hybrid Layer-by-Layer Coatings. *ACS Applied Materials & Interfaces* **2017**, *9* (34), 29082–29092. <https://doi.org/10.1021/acsami.7b08018>.
- (121) Köklükaya, O.; Carosio, F.; Wågberg, L. Tailoring Flame-Retardancy and Strength of Papers via Layer-by-Layer Treatment of Cellulose Fibers. *Cellulose* **2018**, *25* (4), 2691–2709. <https://doi.org/10.1007/s10570-018-1749-8>.
- (122) Carosio, F.; Di Blasio, A.; Alongi, J.; Malucelli, G. Layer by Layer Nanoarchitectures for the Surface Protection of Polycarbonate. *European Polymer Journal* **2013**, *49* (2), 397–404. <https://doi.org/10.1016/j.eurpolymj.2012.10.032>.
- (123) Laachachi, A.; Ball, V.; Apaydin, K.; Toniazzi, V.; Ruch, D. Diffusion of Polyphosphates into (Poly(Allylamine)-Montmorillonite) Multilayer Films: Flame Retardant-Intumescent Films with Improved Oxygen Barrier. *Langmuir* **2011**, *27* (22), 13879–13887. <https://doi.org/10.1021/la203252q>.
- (124) Apaydin, K.; Laachachi, A.; Ball, V.; Jimenez, M.; Bourbigot, S.; Toniazzi, V.; Ruch, D. Polyallylamine-Montmorillonite as Super Flame Retardant Coating Assemblies by Layer-by Layer Deposition on Polyamide. *Polymer Degradation and Stability* **2013**, *98* (2), 627–634. <https://doi.org/10.1016/j.polymdegradstab.2012.11.006>.
- (125) Guin, T.; Kreckler, M.; Milhorn, A.; Hagen, D. A.; Stevens, B.; Grunlan, J. C. Exceptional Flame Resistance and Gas Barrier with Thick Multilayer Nanobrick Wall Thin Films. *Advanced Materials Interfaces* **2015**, *2* (11), 1500214. <https://doi.org/10.1002/admi.201500214>.
- (126) Fu, J.; Schlenoff, J. B. Driving Forces for Oppositely Charged Polyion Association in Aqueous Solutions: Enthalpic, Entropic, but Not Electrostatic. *Journal of the American Chemical Society* **2016**, *138* (3), 980–990. <https://doi.org/10.1021/jacs.5b11878>.
- (127) Mattison, K. W.; Dubin, P. L.; Brittain, I. J. Complex Formation between Bovine Serum Albumin and Strong Polyelectrolytes: Effect of Polymer Charge Density. *The Journal of Physical Chemistry B* **1998**, *102* (19), 3830–3836. <https://doi.org/10.1021/jp980486u>.
- (128) Chen, J.; Heitmann, J. A.; Hubbe, M. A. Dependency of Polyelectrolyte Complex Stoichiometry on the Order of Addition. 1. Effect of Salt Concentration during Streaming Current Titrations with Strong Poly-Acid and Poly-Base. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2003**, *223* (1–3), 215–230. [https://doi.org/10.1016/S0927-7757\(03\)00222-X](https://doi.org/10.1016/S0927-7757(03)00222-X).
- (129) de Vasconcelos, C. L.; Bezerril, P. M.; dos Santos, D. E. S.; Dantas, T. N. C.; Pereira, M. R.; Fonseca, J. L. C. Effect of Molecular Weight and Ionic Strength on the Formation of Polyelectrolyte Complexes Based on Poly(Methacrylic Acid) and Chitosan. *Biomacromolecules* **2006**, *7* (4), 1245–1252. <https://doi.org/10.1021/bm050963w>.
- (130) Chollakup, R.; Beck, J. B.; Dirnberger, K.; Tirrell, M.; Eisenbach, C. D. Polyelectrolyte Molecular Weight and Salt Effects on the Phase Behavior and Coacervation of Aqueous Solutions of Poly(Acrylic Acid) Sodium Salt and Poly(Allylamine) Hydrochloride. *Macromolecules* **2013**, *46* (6), 2376–2390. <https://doi.org/10.1021/ma202172q>.

- (131) Lounis, F. M.; Chamieh, J.; Leclercq, L.; Gonzalez, P.; Geneste, A.; Prelot, B.; Cottet, H. Interactions between Oppositely Charged Polyelectrolytes by Isothermal Titration Calorimetry: Effect of Ionic Strength and Charge Density. *The Journal of Physical Chemistry B* **2017**, *121* (12), 2684–2694. <https://doi.org/10.1021/acs.jpcc.6b11907>.
- (132) Cain, A. A.; Murray, S.; Holder, K. M.; Nolen, C. R.; Grunlan, J. C. Intumescent Nanocoating Extinguishes Flame on Fabric Using Aqueous Polyelectrolyte Complex Deposited in Single Step: Intumescent Nanocoating Extinguishes Flame on Fabric. *Macromolecular Materials and Engineering* **2014**, *299* (10), 1180–1187. <https://doi.org/10.1002/mame.201400022>.
- (133) Haile, M.; Fincher, C.; Fomete, S.; Grunlan, J. C. Water-Soluble Polyelectrolyte Complexes That Extinguish Fire on Cotton Fabric When Deposited as PH-Cured Nanocoating. *Polymer Degradation and Stability* **2015**, *114*, 60–64. <https://doi.org/10.1016/j.polymdegradstab.2015.01.022>.
- (134) Palen, B.; Rabaey, M. G.; Rodriguez-Melendez, D.; Iverson, E. T.; Kolibaba, T. J.; Grunlan, J. C. Polymeric Coacervate Coating for Flame Retardant Paper. *Cellulose* **2022**, *29* (8), 4589–4597. <https://doi.org/10.1007/s10570-022-04594-7>.
- (135) Kolibaba, T. J.; Vest, N. A.; Grunlan, J. C. Polyelectrolyte Photopolymer Complexes for Flame Retardant Wood. *Materials Chemistry Frontiers* **2022**, *6*, 1630–1636. <https://doi.org/10.1039/D2QM00257D>.
- (136) Jimenez, M.; Guin, T.; Bellayer, S.; Dupretz, R.; Bourbigot, S.; Grunlan, J. C. Microintumescent Mechanism of Flame-Retardant Water-Based Chitosan-Ammonium Polyphosphate Multilayer Nanocoating on Cotton Fabric. *Journal of Applied Polymer Science* **2016**, *133* (32), 43783. <https://doi.org/10.1002/app.43783>.
- (137) Leistner, M.; Haile, M.; Rohmer, S.; Abu-Odeh, A.; Grunlan, J. C. Water-Soluble Polyelectrolyte Complex Nanocoating for Flame Retardant Nylon-Cotton Fabric. *Polymer Degradation and Stability* **2015**, *122*, 1–7. <https://doi.org/10.1016/j.polymdegradstab.2015.10.008>.
- (138) Haile, M.; Leistner, M.; Sarwar, O.; Toler, C. M.; Henderson, R.; Grunlan, J. C. A Wash-Durable Polyelectrolyte Complex That Extinguishes Flames on Polyester–Cotton Fabric. *RSC Advances* **2016**, *6* (40), 33998–34004. <https://doi.org/10.1039/C6RA03637F>.
- (139) Li, L.; Qi, P.; Peng, A.; Sun, J.; Cui, Z.; Liu, W.; Li, H.; Gu, X.; Zhang, S. Preparation of Durable Flame Retardant Nylon-Cotton Blend Fabrics by 3-Glycidyloxypropyl Trimethoxy Silane Associated with Polyethyleneimine and Phytic Acid. *Cellulose* **2022**, *29* (13), 7413–7430. <https://doi.org/10.1007/s10570-022-04693-5>.
- (140) Cheng, X.-W.; Guan, J.-P.; Yang, X.-H.; Tang, R.-C.; Yao, F. A Bio-Resourced Phytic Acid/Chitosan Polyelectrolyte Complex for the Flame Retardant Treatment of Wool Fabric. *Journal of Cleaner Production* **2019**, *223*, 342–349. <https://doi.org/10.1016/j.jclepro.2019.03.157>.
- (141) Wang, Z.-H.; Zhang, A.-N.; Liu, B.-W.; Wang, X.-L.; Zhao, H.-B.; Wang, Y.-Z. Durable Flame-Retardant Cotton Fabrics with Tannic Acid Complexed by Various Metal Ions. *Polymer Degradation and Stability* **2022**, *201*, 109997. <https://doi.org/10.1016/j.polymdegradstab.2022.109997>.
- (142) He, J.-L.; Luo, W.; Wang, T.; He, L.; Deng, J.-N.; Fu, Z.-C.; Grunlan, J. C.; Chen, M.-J. Polyelectrolyte Complex with Controllable Viscosity by Doping Cu<sup>2+</sup> Protects Nylon–Cotton Fabric against Fire. *ACS Applied Materials & Interfaces* **2022**, *14* (48), 54225–54232. <https://doi.org/10.1021/acsmi.2c16343>.
- (143) Carosio, F.; Alongi, J. Flame Retardant Multilayered Coatings on Acrylic Fabrics Prepared by One-Step Deposition of Chitosan/Montmorillonite Complexes. *Fibers* **2018**, *6* (2), 36. <https://doi.org/10.3390/fib6020036>.
- (144) Kundu, C. K.; Wang, X.; Song, L.; Hu, Y. Chitosan-Based Flame Retardant Coatings for Polyamide 66 Textiles: One-Pot Deposition versus Layer-by-Layer Assembly. *International Journal of Biological Macromolecules* **2020**, *143*, 1–10. <https://doi.org/10.1016/j.ijbiomac.2019.11.220>.
- (145) Rao, W.; Shi, J.; Yang, M.; Yang, F.; Wu, T.; Yu, C.; Chen, M.-J.; Zhao, H.-B. One-Pot Fabrication of Bio-Based Hydrophobic and Flame-Retardant Coating for Cotton Fabric. *Cellulose* **2023**, *30* (3), 1943–1955. <https://doi.org/10.1007/s10570-022-05005-7>.
- (146) Wang, T.; Xu, J.; Zhan, Y.-J.; He, L.; Deng, J.; Fu, Z.-C.; Zhao, H.-B.; Chen, M.-J. Eco-Friendly and Facile Integrated Intumescent Polyelectrolyte Complex Coating with Universal Flame Retardancy and Smoke Suppression for Cotton and Its Blending Fabrics. *ACS Sustainable Chemistry & Engineering* **2023**, *11* (12), 4838–4849. <https://doi.org/10.1021/acssuschemeng.3c00028>.
- (147) Papo, A.; Piani, L.; Ricceri, R. Sodium Tripolyphosphate and Polyphosphate as Dispersing Agents for Kaolin Suspensions: Rheological Characterization. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2002**, *201* (1–3), 219–230. [https://doi.org/10.1016/S0927-7757\(01\)01024-X](https://doi.org/10.1016/S0927-7757(01)01024-X).
- (148) Palen, B.; Kolibaba, T. J.; Brehm, J. T.; Shen, R.; Quan, Y.; Wang, Q.; Grunlan, J. C. Clay-Filled Polyelectrolyte Complex Nanocoating for Flame-Retardant Polyurethane Foam. *ACS Omega* **2021**, *6* (12), 8016–8020. <https://doi.org/10.1021/acsomega.0c05354>.
- (149) Meng, D.; Liu, X.; Wang, S.; Sun, J.; Li, H.; Wang, Z.; Gu, X.; Zhang, S. Self-Healing Polyelectrolyte Complex Coating for Flame Retardant Flexible Polyurethane Foam with Enhanced Mechanical Property. *Composites Part B: Engineering* **2021**, *219*, 108886. <https://doi.org/10.1016/j.compositesb.2021.108886>.
- (150) Bellanger, H.; Casdorff, K.; Muff, L. F.; Ammann, R.; Burgert, I.; Michen, B. Layer-by-Layer Deposition on a Heterogeneous Surface: Effect of Sorption Kinetics on the Growth of Polyelectrolyte Multilayers. *Journal of Colloid and Interface Science* **2017**, *500*, 133–141. <https://doi.org/10.1016/j.jcis.2017.02.048>.
- (151) Kolibaba, T. J.; Grunlan, J. C. Environmentally Benign Polyelectrolyte Complex That Renders Wood Flame Retardant and Mechanically Strengthened. *Macromolecular Materials and Engineering* **2019**, *304* (8), 1900179. <https://doi.org/10.1002/mame.201900179>.
- (152) Soula, M.; Samyn, F.; Duquesne, S.; Landry, V. Innovative Polyelectrolyte Treatment to Flame-Retard Wood. *Polymers* **2021**, *13* (17), 2884. <https://doi.org/10.3390/polym13172884>.
- (153) Gao, S.; Qi, J.; Qi, P.; Xu, R.; Wu, T.; Zhang, B.; Huang, J.; Yan, Y. Unprecedented Nonflammable Organic Adhesives Leading to Fireproof Wood Products. *ACS Applied Materials & Interfaces* **2023**, *15* (6), 8609–8616. <https://doi.org/10.1021/acsmi.2c19072>.
- (154) Fisher, S. G.; Rodriguez-Melendez, D.; Iverson, E. T.; Kolibaba, T. J.; Grunlan, J. C. Fire Protection of Wood with an Environmentally Benign UV-Cured Polyelectrolyte Complex. *Polymer Degradation and Stability* **2023**, 110467. <https://doi.org/10.1016/j.polymdegradstab.2023.110467>.
- (155) Danks, A. E.; Hall, S. R.; Schnepf, Z. The Evolution of ‘Sol–Gel’ Chemistry as a Technique for Materials Synthesis. *Materials Horizons* **2016**, *3* (2), 91–112.
- (156) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic Press: Cambridge, MA, **2013**.

- (157) Hench, L. L.; West, J. K. The Sol-Gel Process. *Chemical Reviews* **1990**, *90* (1), 33–72.
- (158) Avnir, D.; Coradin, T.; Lev, O.; Livage, J. Recent Bio-Applications of Sol-Gel Materials. *Journal of Materials Chemistry* **2006**, *16* (11), 1013–1030.
- (159) Figueira, R. B. Hybrid Sol-Gel Coatings for Corrosion Mitigation: A Critical Review. *Polymers* **2020**, *12* (3), 689.
- (160) Mackenzie, J. D.; Bescher, E. P. Physical Properties of Sol-Gel Coatings. *Journal of Sol-Gel Science and Technology* **2000**, *19*, 23–29.
- (161) Wicks, G. G. *Ceramic Composite Coatings*; Du Pont de Nemours (EI) and Co.: Aiken, SC, **1991**.
- (162) Holman, M. E. Gel-Coated Materials with Increased Flame Retardancy. US 6,696,145 B2, February 24, **2004**. <https://patentimages.storage.googleapis.com/6e/ed/2c/da2ab6b183f58f/US6696145.pdf>.
- (163) Bifulco, A.; Imparato, C.; Aronne, A.; Malucelli, G. Flame Retarded Polymer Systems Based on the Sol-Gel Approach: Recent Advances and Future Perspectives. *Journal of Sol-Gel Science and Technology* **2022**, 1–25.
- (164) Periyasamy, A. P.; Venkataraman, M.; Kremenakova, D.; Militky, J.; Zhou, Y. Progress in Sol-Gel Technology for the Coatings of Fabrics. *Materials* **2020**, *13* (8), 1838.
- (165) Kakihana, M. Invited Review “Sol-Gel” Preparation of High Temperature Superconducting Oxides. *Journal of Sol-Gel Science and Technology* **1996**, *6*, 7–55.
- (166) Ebelmen. Untersuchungen Über Die Verbindungen Der Borsäure Und Kieselsäure Mit Aether. *Justus Liebigs Annalen der Chemie* **1846**, *57* (3), 319–355.
- (167) Mazdiyasi, K. S.; Brown, L. M. Synthesis and Some Properties of Yttrium and Lanthanide Isopropoxides. *Inorganic Chemistry* **1970**, *9* (12), 2783–2786.
- (168) Turova, N. Y.; Korolev, A. V.; Tchebukov, D. E.; Belokon, A. I.; Yanovsky, A. I.; Struchkov, Y. T. Tantalum (V) Alkoxides: Electrochemical Synthesis, Mass-Spectral Investigation and Oxoalkoxocomplexes. *Polyhedron* **1996**, *15* (21), 3869–3880.
- (169) Livage, J.; Henry, M.; Sanchez, C. Sol-Gel Chemistry of Transition Metal Oxides. *Progress in Solid State Chemistry* **1988**, *18* (4), 259–341.
- (170) Guglielmi, M.; Carturan, G. Precursors for Sol-Gel Preparations. *Journal of Non-Crystalline Solids* **1988**, *100* (1–3), 16–30.
- (171) Stöber, W.; Fink, A.; Bohn, E. Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range. *Journal of Colloid and Interface Science* **1968**, *26* (1), 62–69.
- (172) Sui, R.; Charpentier, P. Synthesis of Metal Oxide Nanostructures by Direct Sol-Gel Chemistry in Supercritical Fluids. *Chemical Reviews* **2012**, *112* (6), 3057–3082.
- (173) Pirzada, T.; Ashrafi, Z.; Xie, W.; Khan, S. A. Cellulose Silica Hybrid Nanofiber Aerogels: From Sol-Gel Electrospun Nanofibers to Multifunctional Aerogels. *Advanced Functional Materials* **2020**, *30* (5), 1907359.
- (174) Loy, D. A.; Russick, E. M.; Yamanaka, S. A.; Baugher, B. M.; Shea, K. J. Direct Formation of Aerogels by Sol-Gel Polymerizations of Alkoxysilanes in Supercritical Carbon Dioxide. *Chemistry of Materials* **1997**, *9* (11), 2264–2268.
- (175) Alongi, J.; Ciobanu, M.; Tata, J.; Carosio, F.; Malucelli, G. Thermal Stability and Flame Retardancy of Polyester, Cotton, and Relative Blend Textile Fabrics Subjected to Sol-Gel Treatments. *Journal of Applied Polymer Science* **2011**, *119* (4), 1961–1969.
- (176) Alongi, J.; Ciobanu, M.; Malucelli, G. Sol-Gel Treatments on Cotton Fabrics for Improving Thermal and Flame Stability: Effect of the Structure of the Alkoxysilane Precursor. *Carbohydrate Polymers* **2012**, *87* (1), 627–635.
- (177) Alongi, J.; Ciobanu, M.; Malucelli, G. Thermal Stability, Flame Retardancy and Mechanical Properties of Cotton Fabrics Treated with Inorganic Coatings Synthesized through Sol-Gel Processes. *Carbohydrate Polymers* **2012**, *87* (3), 2093–2099.
- (178) Cireli, A.; Onar, N.; Ebeoglugil, M. F.; Kayatekin, I.; Kutlu, B.; Culha, O.; Celik, E. Development of Flame Retardancy Properties of New Halogen-free Phosphorous Doped SiO<sub>2</sub> Thin Films on Fabrics. *Journal of Applied Polymer Science* **2007**, *105* (6), 3748–3756.
- (179) Yaman, N. Preparation and Flammability Properties of Hybrid Materials Containing Phosphorous Compounds via Sol-Gel Process. *Fibers and Polymers* **2009**, *10* (4), 413–418.
- (180) Alongi, J.; Ciobanu, M.; Malucelli, G. Novel Flame Retardant Finishing Systems for Cotton Fabrics Based on Phosphorus-Containing Compounds and Silica Derived from Sol-Gel Processes. *Carbohydrate Polymers* **2011**, *85* (3), 599–608.
- (181) Brancatelli, G.; Colleoni, C.; Massafra, M. R.; Rosace, G. Effect of Hybrid Phosphorous-Doped Silica Thin Films Produced by Sol-Gel Method on the Thermal Behavior of Cotton Fabrics. *Polymer Degradation and Stability* **2011**, *96* (4), 483–490.
- (182) Cheng, X.-W.; Liang, C.-X.; Guan, J.-P.; Yang, X.-H.; Tang, R.-C. Flame Retardant and Hydrophobic Properties of Novel Sol-Gel Derived Phytic Acid/Silica Hybrid Organic-Inorganic Coatings for Silk Fabric. *Applied Surface Science* **2018**, *427*, 69–80.
- (183) Cheng, X.-W.; Tang, R.-C.; Guan, J.-P.; Zhou, S.-Q. An Eco-Friendly and Effective Flame Retardant Coating for Cotton Fabric Based on Phytic Acid Doped Silica Sol Approach. *Progress in Organic Coatings* **2020**, *141*, 105539.
- (184) Grancaric, A. M.; Colleoni, C.; Guido, E.; Botteri, L.; Rosace, G. Thermal Behaviour and Flame Retardancy of Monoethanolamine-Doped Sol-Gel Coatings of Cotton Fabric. *Progress in Organic Coatings* **2017**, *103*, 174–181.
- (185) Nie, S.; Jin, D.; Yang, J.; Dai, G.; Luo, Y. Fabrication of Environmentally-Benign Flame Retardant Cotton Fabrics with Hydrophobicity by a Facile Chemical Modification. *Cellulose* **2019**, *26*, 5147–5158.
- (186) Lin, D.; Zeng, X.; Li, H.; Lai, X.; Wu, T. One-Pot Fabrication of Superhydrophobic and Flame-Retardant Coatings on Cotton Fabrics via Sol-Gel Reaction. *Journal of Colloid and Interface Science* **2019**, *533*, 198–206.
- (187) Bentis, A.; Boukhriss, A.; Gmouh, S. Flame-Retardant and Water-Repellent Coating on Cotton Fabric by Titania-Boron Sol-Gel Method. *Journal of Sol-Gel Science and Technology* **2020**, *94*, 719–730.
- (188) Vasiljević, J.; Hadžić, S.; Jerman, I.; Černe, L.; Tomšič, B.; Medved, J.; Godec, M.; Orel, B.; Simončič, B. Study of Flame-Retardant Finishing of Cellulose Fibres: Organic-Inorganic Hybrid versus Conventional Organophosphonate. *Polymer Degradation and Stability* **2013**, *98* (12), 2602–2608.
- (189) Liu, Y.; Pan, Y.-T.; Wang, X.; Acuña, P.; Zhu, P.; Wagenknecht, U.; Heinrich, G.; Zhang, X.-Q.; Wang, R.; Wang, D.-Y. Effect of Phosphorus-Containing Inorganic-Organic Hybrid Coating on the Flammability of Cotton Fabrics: Synthesis, Characterization and Flammability. *Chemical Engineering Journal* **2016**, *294*, 167–175.
- (190) Castellano, A.; Colleoni, C.; Iacono, G.; Mezzi, A.; Plutino, M. R.; Malucelli, G.; Rosace, G. Synthesis and Characterization of a Phosphorous/Nitrogen Based Sol-Gel Coating as a Novel Halogen- and Formaldehyde-Free

- Flame Retardant Finishing for Cotton Fabric. *Polymer Degradation and Stability* **2019**, *162*, 148–159.
- (191) Yang, Z.; Fei, B.; Wang, X.; Xin, J. H. A Novel Halogen-free and Formaldehyde-free Flame Retardant for Cotton Fabrics. *Fire and Materials* **2012**, *36* (1), 31–39.
- (192) Šehić, A.; Tomšič, B.; Jerman, I.; Vasiljević, J.; Medved, J.; Simončič, B. Synergistic Inhibitory Action of P- and Si-Containing Precursors in Sol–Gel Coatings on the Thermal Degradation of Polyamide 6. *Polymer Degradation and Stability* **2016**, *128*, 245–252.
- (193) Vasiljević, J.; Tomšič, B.; Jerman, I.; Orel, B.; Jakša, G.; Kovač, J.; Simončič, B. Multifunctional Superhydrophobic/Oleophobic and Flame-Retardant Cellulose Fibres with Improved Ice-Releasing Properties and Passive Antibacterial Activity Prepared via the Sol–Gel Method. *Journal of Sol-Gel Science and Technology* **2014**, *70*, 385–399.
- (194) Qi, L.; Qiu, S.; Xi, J.; Yu, B.; Hu, Y.; Xing, W. Construction of Super-Hydrophobic, Highly Effective Flame Retardant Coating for Cotton Fabric with Superior Washability and Abrasion Resistance. *Journal of Colloid and Interface Science* **2022**, *607*, 2019–2028.
- (195) Bellayer, S.; Jimenez, M.; Barrau, S.; Bourbigot, S. Fire Retardant Sol–Gel Coatings for Flexible Polyurethane Foams. *RSC Advances* **2016**, *6* (34), 28543–28554.
- (196) Bellayer, S.; Jimenez, M.; Prieur, B.; Dewailly, B.; Ramgobin, A.; Sarazin, J.; Revel, B.; Tricot, G.; Bourbigot, S. Fire Retardant Sol-Gel Coated Polyurethane Foam: Mechanism of Action. *Polymer Degradation and Stability* **2018**, *147*, 159–167.
- (197) Shi, Y.; Wang, N.; Liu, L.; Liu, Y. Surface Sedimentation and Adherence of Nano-SiO<sub>2</sub> to Improve Thermal Stability and Flame Resistance of Melamine-formaldehyde Foam via Sol-gel Method. *Fire and Materials* **2018**, *42* (2), 183–189.
- (198) Bo, G.; Xu, X.; Tian, X.; Wu, J.; He, X.; Xu, L.; Yan, Y. Enhancing the Flame Retardancy for Castor Oil-Based Rigid Polyurethane Foams via Silica Aerogel. *Journal of Non-Crystalline Solids* **2021**, *562*, 120783.
- (199) Qu, L.; Rahimi, S.; Qian, J.; He, L.; He, Z.; Yi, S. Preparation and Characterization of Hydrophobic Coatings on Wood Surfaces by a Sol-Gel Method and Post-Aging Heat Treatment. *Polymer Degradation and Stability* **2021**, *183*, 109429.
- (200) Shabir Mahr, M.; Hübert, T.; Sabel, M.; ScharTEL, B.; Bahr, H.; Militz, H. Fire Retardancy of Sol–Gel Derived Titania Wood-Inorganic Composites. *Journal of Materials Science* **2012**, *47*, 6849–6861.
- (201) Bellayer, S.; Gossiaux, A.; Duquesne, S.; Dewailly, B.; Bachelet, P.; Jimenez, M. Transparent Fire Protective Sol-Gel Coating for Wood Panels. *Polymer Testing* **2022**, *110*, 107579.
- (202) Zille, A.; Oliveira, F. R.; Souto, A. P. Plasma Treatment in Textile Industry: Plasma Treatment in Textile Industry. *Plasma Processes and Polymers* **2015**, *12* (2), 98–131. <https://doi.org/10.1002/ppap.201400052>.
- (203) Tudoran, C.; Roşu, M.; Coroş, M. A Concise Overview on Plasma Treatment for Application on Textile and Leather Materials. *Plasma Processes and Polymers* **2020**, *17* (8), 2000046. <https://doi.org/10.1002/ppap.202000046>.
- (204) Bell, A. T. The Mechanism and Kinetics of Plasma Polymerization. In *Plasma Chemistry III*; Vepřek, S., Venugopalan, M., Eds.; Topics in Current Chemistry; Springer-Verlag: Berlin and Heidelberg, **1980**; Vol. 94, pp 43–68. <https://doi.org/10.1007/BFb0048586>.
- (205) Horrocks, A.; Eivazi, S.; Ayesh, M.; Kandola, B. Environmentally Sustainable Flame Retardant Surface Treatments for Textiles: The Potential of a Novel Atmospheric Plasma/UV Laser Technology. *Fibers* **2018**, *6* (2), 31. <https://doi.org/10.3390/fib6020031>.
- (206) Jang, H. J.; Jung, E. Y.; Parsons, T.; Tae, H.-S.; Park, C.-S. A Review of Plasma Synthesis Methods for Polymer Films and Nanoparticles under Atmospheric Pressure Conditions. *Polymers* **2021**, *13* (14), 2267. <https://doi.org/10.3390/polym13142267>.
- (207) Akovali, G.; Gundogan, G. Studies on Flame Retardancy of Polyacrylonitrile Fiber Treated by Flame-Retardant Monomers in Cold Plasma. *Journal of Applied Polymer Science* **1990**, *41* (910), 2011–2019. <https://doi.org/10.1002/app.1990.070410907>.
- (208) Bourbigot, S.; Charaffedine, J.; Le Bras, M.; Delobel, R.; Dessaux, O.; Goudmand, P. New Approach to Flame Retardancy Using Plasma Assisted Surface Polymerisation Techniques. *Polymer Degradation and Stability* **1999**, *66*, 153–155.
- (209) ScharTEL, B.; Kühn, G.; Mix, R.; Friedrich, J. Surface Controlled Fire Retardancy of Polymers Using Plasma Polymerisation. *Macromolecular Materials and Engineering* **2002**, *287*, 579–582.
- (210) Tsafack, M. J.; Levalois-Grützmaier, J. Towards Multifunctional Surfaces Using the Plasma-Induced Graft-Polymerization (PIGP) Process: Flame and Waterproof Cotton Textiles. *Surface and Coatings Technology* **2007**, *201* (12), 5789–5795. <https://doi.org/10.1016/j.surfcoat.2006.10.027>.
- (211) Kamlangkla, K.; Hodak, S. K.; Levalois-Grützmaier, J. Multifunctional Silk Fabrics by Means of the Plasma Induced Graft Polymerization (PIGP) Process. *Surface and Coatings Technology* **2011**, *205* (13–14), 3755–3762. <https://doi.org/10.1016/j.surfcoat.2011.01.006>.
- (212) Horrocks, A. R.; Nazaré, S.; Masood, R.; Kandola, B.; Price, D. 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* **2011**, *22* (1), 22–29. <https://doi.org/10.1002/pat.1707>.
- (213) Carosio, F.; Alongi, J.; Frache, A. Influence of Surface Activation by Plasma and Nanoparticle Adsorption on the Morphology, Thermal Stability and Combustion Behavior of PET Fabrics. *European Polymer Journal* **2011**, *47* (5), 893–902. <https://doi.org/10.1016/j.eurpolymj.2011.01.009>.
- (214) Caschera, D.; Toro, R. G.; Federici, F.; Riccucci, C.; Ingo, G. M.; Gigli, G.; Cortese, B. Flame Retardant Properties of Plasma Pre-Treated/Diamond-Like Carbon (DLC) Coated Cotton Fabrics. *Cellulose* **2015**, *22* (4), 2797–2809. <https://doi.org/10.1007/s10570-015-0661-8>.
- (215) Ayesh, M.; Horrocks, A. R.; Kandola, B. K. The Effect of Combined Atmospheric Plasma/UV Treatments on Improving the Durability of Flame Retardants Applied to Cotton. *Molecules* **2022**, *27* (24), 8737. <https://doi.org/10.3390/molecules27248737>.
- (216) Qi, L.; Wang, B.; Zhang, W.; Yu, B.; Zhou, M.; Hu, Y.; Xing, W. Durable Flame Retardant and Dip-Resistant Coating of Polyester Fabrics by Plasma Surface Treatment and UV-Curing. *Progress in Organic Coatings* **2022**, *172*, 107066. <https://doi.org/10.1016/j.porgcoat.2022.107066>.
- (217) Jimenez, M.; Lesaffre, N.; Bellayer, S.; Dupretz, R.; Vandenbossche, M.; Duquesne, S.; Bourbigot, S. Novel Flame Retardant Flexible Polyurethane Foam: Plasma Induced Graft-Polymerization of Phosphonates. *RSC Advances* **2015**, *5* (78), 63853–63865. <https://doi.org/10.1039/C5RA08289G>.