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*Chapter*

**LAYER-BY-LAYER: AN EFFECTIVE SURFACE  
ENGINEERED STRATEGY FOR FLAME  
RETARDANT TEXTILES**

***Giulio Malucelli\****

Department of Applied Science and Technology,  
Politecnico di Torino, Torino, Italy

**ABSTRACT**

This chapter reviews the current state of the art about the use of the layer-by-layer (LbL) strategy for providing natural and synthetic textile materials with flame retardant properties. Among the surface engineered approaches, this technique has attracted the interest of several research groups, because of its simplicity, the low environmental impact of the employed components and the possibility, almost infinite, to tailor the surface properties, including flame retardancy, of the layer-by-layer treated substrates. Besides, the possibility of setting pilot or semi-pilot plants for depositing LbL assemblies on different textiles opens the way towards the future possible industrialization of the method. This chapter reviews and

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\* Corresponding Author Email: [giulio.malucelli@polito.it](mailto:giulio.malucelli@polito.it).

discusses the current advances, highlighting the still open challenges and future possible developments.

**Keywords:** layer-by-layer, textiles, flame retardancy, flame retardants, biomacromolecules, flame spread tests, forced-combustion tests, durability

## INTRODUCTION

The ease of **flammability** of textiles represents a very important concern for their possible exploitation in different application fields. In fact, if not intrinsically resistant to fire (i.e., intrinsically fire or **flame retardant**), both natural and synthetic fabrics easily ignite when exposed to an **irradiative heat flux** or a **flame**. Besides, synthetic fabrics, during the combustion, may exhibit **melt dripping** phenomena: this way, the formed incandescent drops may further favor the flame propagation to other flammable materials, hence worsening the fire hazards [1-3].

In this context, **textiles** (either in form of fibers, or fabrics) need to be fire or flame retarded: in other words, they require some physical or chemical treatments, in order to be capable to delay the flame propagation (**fire retardant** textiles) or to stop it (**flame retardant** textiles). Apart from some synthetic polymers used in textile technology, for which it is possible to incorporate specific flame retardant additives by compounding prior to spinning processes, providing flame retardancy to textiles is a big challenging issue, as their morphology is very peculiar and irregular. Therefore, both academic and industrial research has been focused on the design and development of surface engineered methods, based on the physical or chemical deposition of flame retardant additives on the fiber/fabric surface [4].

These techniques comprise **sol-gel processes**, (nano)particle absorption [5], plasma treatments [6], as well as the **layer-by-layer** (LbL) approach that represents a novel and powerful method for designing fully inorganic, fully organic or hybrid organic/inorganic coatings on the textile surface. LbL has

been successfully employed for conferring (multi)functional properties to either natural or synthetic textiles, plastic thin films, expanded foams. In this chapter, a comprehensive description of the use of the layer-by-layer approach for conferring flame retardant features to textiles will be carried out, focusing on the very recent developments, discussing the current pros and cons, highlighting some possible perspectives for this surface engineered technique for the very next future.

## **HISTORY, FUNDAMENTALS AND DEVELOPMENTS OF THE LAYER-BY-LAYER TECHNIQUE**

The Layer-by-Layer (LbL) technique is not new at all, as it dates back to the 1960s, thanks to the pioneering studies carried out by Iler [7], who first demonstrated the potential of the method, suitable for fabricating nanostructured coatings by means of a molecularly-controlled process. Unexpectedly, the proposed surface engineered technique was not successfully exploited until the early 1990s, when Decher proposed a practical approach suitable for obtaining assemblies made of layers of polyanions and polycations on a substrate [8].

Nowadays, LbL is gaining popularity and is stimulating both academic and industrial researchers to thoroughly investigate its great potential, derived from either the possibility of combining really an limitless number of constituents of the deposited layers or the related functionalities. Hence, it is now possible to design multifunctional **layer-by-layer assemblies** that, in a very limited thickness, can provide the underlying coated substrate with specific features, without impacting on its bulk behavior [9-11].

In order to build a LbL assembly, first the substrate to treat, which is weakly electrically charged (usually with a negative charge), has to be exposed to water-based suspensions/solutions that comprise micro- or nanoparticles or **polyelectrolytes**, respectively. To this aim, **spraying** or **dipping** techniques can be utilized; usually spraying is preferable when the process has to be performed on a pilot/industrial scale, while dipping is more suitable

for lab-scale operations. Each dipping or spraying step may take from seconds to minutes, depending on the type of deposited layer and on the adopted experimental conditions (as an examples, rinsing intermediate steps can be adopted). In fact, it is possible to rinse and dry the treated substrate after each deposition step; this is usually carried out with two main objectives: i) to remove any inaccurately adhered material and ii) to prevent possible contaminations occurring between the oppositely charged suspensions/solutions, hence prolonging the lifetime of the polyelectrolytes/particles baths. The reversal of the surface charges induced by the consecutive depositions of the layers allows the formation of growing assemblies electrostatically bonded. The deposition process can continue until the desired number of deposited layers is achieved; usually, also depending on the type and structure of the assemblies, 10 to 50 layers can be easily deposited on different substrates (plastics, metals, wood).

Electrostatic interactions are not the only possible way for bonding the deposited layers, hence creating a “strong” and stable assembly: in fact, it is possible to exploit the formation of covalent bonds [12, 13], hydrogen bonding [14, 15], donor/acceptor interactions [16, 17], stereocomplex formation [18, 19], among a few to mention.

A scheme of an LbL deposition process is shown in Figure 1.

As components of the LbL assembly, it is possible to utilize different cationic or anionic polyelectrolytes [20-22], layered silicates [23-25], metallic or oxidic colloids [26-29], among a few to mention. Furthermore, the layer-by layer deposition process, as well as the morphology of the final resulting assemblies are remarkably influenced by the adopted experimental conditions. In particular, the process is strictly dependent on several factors, namely:

- the pH of the solutions/suspensions [30, 31]
- the chemical structure [32] and the molecular weight [33] of the employed polyelectrolytes
- the deposition temperature [34]
- the adsorption time [35]
- the possible drying step [36]

- the types of counterions [37]
- the ionic strength [38].

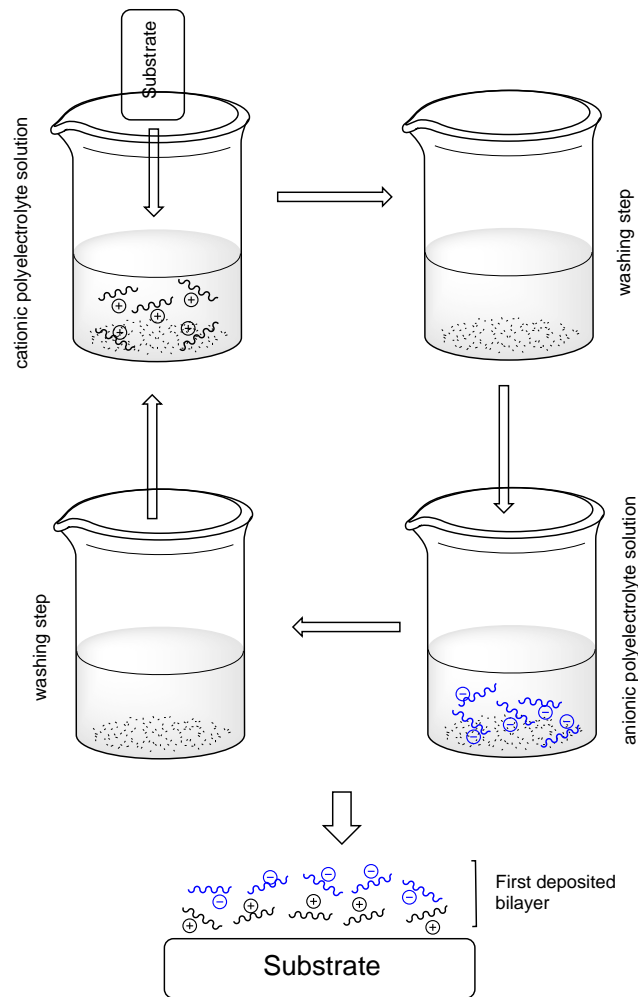


Figure 1. Layer-by-layer through dipping a generic substrate into baths containing polyelectrolytes: scheme of the first two depositions.

The exploitation of the layer-by-layer method for flame retardant purposes started 5 to 10 years ago: from the very beginning, it was clear that this surface engineered strategy is easily employable and suitable for different polymeric materials in form of thin films, fabrics, bulk substrates, expanded polymer structures [39, 40]. The main advantages related to the use of the LbL flame retarded assemblies in comparison with the conventional FR treatments refer to: i) the multifunctional features, apart from flame retardancy, the substrates can be provided with (namely, hydrophobicity, electrical conductivity, antibacterial properties, among a few to mention), ii) the mild conditions selected for its application (i.e., atmospheric pressure and room temperature) and iii) the “green” character of the technique, as it usually utilizes water as a solvent for dissolving or dispersing the **polyelectrolytes** or the **(nano)particles**, respectively. Besides, these solution/suspension baths are very diluted (the concentrations of the LbL constituents are usually kept below 1 wt.%), so that it becomes very easy to recycle them after use.

The first proof concerning the possibility to use LbL assemblies for flame retardant purposes appeared in a pioneering work published in 2006 by Srikulkit et al. [41]: notwithstanding that the fire behavior was not proven by means of specific fire tests, it was demonstrated that bilayered assemblies made of chitosan (positively charged) and polyphosphoric acid (negatively charged) were able to improve the thermal resistance of silk fabrics.

Then, LbL was started to be widely exploited in flame retardancy, according to the design of flame retardant coatings showing thermal shielding features and/or intumescent properties. The former were achieved by designing assemblies made of different types of (nano)particles organized as fully inorganic or hybrid organic-inorganic coatings. In fact, the ceramic phase is able to slow down the oxygen diffusion towards the underlying substrate, as well as to lower the heat transfer during the combustion.

Conversely, **intumescent LbL assemblies** are the newest solution in flame retardant LbL assemblies: generally speaking, the exposure of the treated fabrics to a heat flux or a flame induces the activation/degradation of the assembly, which originates an expanded carbonaceous structure (the so-called **char**), able to exert a certain protection on the underlying material.

The components of an **intumescent LbL assembly** should be specifically selected in order to behave:

- as an acid source that, upon the release of acidic species, is able to favor the dehydration of the fabric, hence giving rise to the formation of the char
- as a carbon source that contributes to the formation of the carbonaceous structure
- as a blowing agent that, upon exposure to a heat flux or a flame, gives rise to the formation of non-combustible swelling species, responsible for the foaming of the char.

It is noteworthy that LbL intumescent coating may also contain ceramic phases, thus combining the thermal shielding effect with the intumescent features in a single hybrid assembly.

In the next paragraphs an overview of the progress of FR layer-by-layer assemblies over the last 10 years will be described.

### **Fully Inorganic LbL Assemblies**

The first paper deals with an assembly made of alternating positive alumina-coated silica (10 nm) and negative **silica nanoparticles** (10 or 40 nm), deposited on cotton fabrics by means of a dipping procedure [42]. In particular, the cellulosic fabric achieved self-extinction in **vertical flame spread tests** when 20 bilayers were utilized; besides, the deposited coating was responsible for an increase of the time to ignition, as assessed by forced-combustion tests.

Pursuing this research, the same layer components were deposited on cotton, replacing dipping with a **spray-assisted layer-by-layer technique**. The spray method performed in horizontal configuration was found to cover surface of the cellulosic substrate more homogeneously as compared to the vertical method; in addition, the horizontal LbL configuration gave the best performances in cone calorimetry tests, confirming the efficiency of the

ceramic assembly in the protection of the fabric when exposed to a heat flux of 35 kW/m<sup>2</sup> [43, 44].

Then, the same assembly was further applied to polycarbonate thin and thick films [45]. In particular, the deposition of 20 bilayers (thickness about 200 nm) on 200 μm polycarbonate films allowed suppressing the melt dripping during vertical flame spread tests; at variance, the performances in forced combustion tests were much better for 5 bilayer assemblies, which determined the highest reduction of peak of heat release rate (pkHRR) and total heat release (THR), significantly increasing, at the same time, the time to ignition (TTI). This behavior was attributed to the higher stability of the 5 bilayer assembly as compared to the 20 bilayer counterpart during cone calorimetry tests.

Silica nanoparticles were not the only constituents of the layer-by-layer assemblies deposited on fabrics: first, by tuning the pH of the dispersions (hence exploiting the amphoteric behavior of the filler), it was possible to build up assemblies made of 50 nm **alumina nanoparticles**, positively or negatively charged, on cotton. The resulting treated fabrics showed an improved flame retardance, as well as enhanced UV-transmittance and tensile strength [46].

Then, many other nanoparticles have been employed for designing fully inorganic layer-by-layer assemblies. More specifically, **Polyhedral Oligomeric Silsesquioxane (POSS®)** salts, bearing a positive or negative electrical charge, were first chosen as constituents of the LbL coatings. The first example deals with the combination of water-soluble OctaTetramethylammonium POSS ((-)POSS) and OctaAmmonium POSS ((+)POSS) in bilayered structures deposited on cotton by means of a dipping process [47]. Aside from the two aforementioned nanoparticles, an aminopropyl silsesquioxane oligomer was also selected as possible constituent substituting the (+)POSS layer. **Micro cone calorimetry tests** showed a significant increase of the char formation (12%) for the LbL-treated fabrics as compared to the untreated counterpart; furthermore, in **vertical flame spread tests**, the afterglow time was lowered and the assembly was capable for maintaining the texture and the shape of individual fibers after burning.

Octapropylammonium-functionalized POSS<sup>®</sup> or alumina-coated silica nanoparticles were exploited as cationic layer and coupled with  $\alpha$ -zirconium phosphate nanoplatelets (as anionic layer) on polyester fabrics [48]. Cone calorimetry tests performed at 35 kW/m<sup>2</sup> heat flux indicated that the deposited coatings were responsible for an increased time to ignition (+42%) and a decreased peak of heat release rate (-16%). Besides, the smoke production rate was significantly lowered (-20%), as well as CO and CO<sub>2</sub> yields (-30 and -45%, respectively).

Quite recently, acrylic fabrics were treated with 4 or 6 bilayers made of ammonium polyphosphate and octapropyl ammonium polyhedral oligomeric silsesquioxane. As demonstrated by horizontal flame spread tests, melt dripping was prevented by the LbL deposition and the combustion rate was remarkably lowered. These findings were interpreted on the basis of the composition of the LbL architectures, where each single layer played a specific role. More specifically, the treated fabrics took advantage from ammonium polyphosphate that behaved as a char former, and from octapropyl ammonium polyhedral oligomeric silsesquioxane, which acted as thermal insulator on the underlying fabric [49].

### Intumescent LbL Assemblies

The very promising FR results coming from fully inorganic assemblies have been exploited as starting point for the design of new LbL intumescent systems, hence combining, in a single coating, the barrier features of the ceramic/inorganic layer with the char-forming properties of the organic reactive intumescent counterpart.

For this purpose, poly(allylamine) (acting as carbon source and blowing agent) and sodium phosphates (acting as acid source) were first LbL-assembled on cotton, exploiting a dipping process [50]. As assessed during vertical flame spread tests, the treated cellulosic substrates achieved self-extinction; besides, it was not possible to ignite the LbL-treated fabrics in forced-combustion tests performed at 35 kW/m<sup>2</sup>. Pursuing this research, a similar assembly was then deposited onto polyamide 6,6 fabrics: micro cone

calorimetry tests highlighted an important decrease of the heat release rate for the treated substrates [51].

Coupling **chitosan** (acting as carbon source) with ammonium polyphosphate (acting as acid source and blowing agent) allowed designing intumescent assemblies on cotton-polyester blends [52]. As assessed by horizontal flame spread tests, the assemblies were able to suppress afterglow phenomena, decreasing the burning rate and leaving, at the same time, a coherent residue.

Then, it was possible to design and deposit a quad-layer LbL assembly made of poly(diallyldimethylammonium chloride)/poly(acrylic acid)/poly(diallyldimethylammonium chloride)/ammonium polyphosphate on **cotton** and on **polyester** fabric substrates [53]. In **horizontal flame spread tests**, the LbL-treated textiles achieved **self-extinction**; referring to polyester fabrics, the deposited assemblies were able to prevent melt dripping phenomena.

**Polyethylenimine** (acting as carbon source) and **ammonium polyphosphate** (acting as acid source and blowing agent) were coupled in a bilayered coating and deposited on ramie fabrics [54]: the flame retardant properties of the treated textiles were studied as a function of polyelectrolyte concentrations, hence of the composition of the deposited assemblies. It was found that those containing high concentrations of ammonium polyphosphate were capable to achieve self-extinction in vertical flame spread tests.

The same fabrics were then LbL-treated with bilayers consisting of **branched polyethylenimine** (used as carbon source and blowing agent) and **poly(vinylphosphonic acid)** (as acid source), in the presence of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  cations [55]. Though it was not possible to provide the fabrics with self-extinction, the transition-metal-ions turned out to lower the combustion time, increasing, at the same time, the final residue. These effects were attributed to the cations that catalyzed the formation of phosphoric acid from poly(vinylphosphonic acid) at low temperatures, hence anticipating the flame retardant activation.

**Graphene oxide** (GO) nanosheets, which are known for possessing barrier properties towards different gases, were coupled with FR

intumescent polyacrylamide layers (obtained from the polymerization reaction of acrylamide with N-(5,5-dimethyl-1,3,2-dioxaphosphinyl-2-yl)-acrylamide [56], thus obtaining an assembly combining platelets with a char-forming polymer. Forced combustion tests highlighted significant improvements in the thermal parameters, with a reduction of both peak of heat release rate (-50%) and total heat release (-22%), as well as an increased time to ignition (+56%).

Quite recently, new LbL assemblies consisting of intumescent layers combined with low environmental impact (bio)macromolecules have been conceived and applied to different fabrics.

The first example reported in the scientific literature deals with bilayered assemblies made of **phytic acid** (acting as an acid source) and **chitosan** (acting as carbon source) and deposited on cotton fabrics [57]. It was possible to achieve self-extinction in vertical flame spread tests by tuning the pH of each dipping bath. More specifically, two pH values were specifically considered: it was found that the assemblies built at pH = 4 were thinner and contained 66 wt.% of phytic acid, while those at pH = 6 were thicker and with 48wt.% of phytic acid.

Among the exploitable low environmental impact biomacromolecules, **deoxyribonucleic acid (DNA)** was coupled with chitosan in bilayered assemblies on **cotton** fabrics [58]. Indeed, thanks to its structure and composition, this biomacromolecule can be considered as an all-in-one intumescent system. In particular, it bears phosphate groups that act as acid source, deoxyribose units that represent a carbon source and nitrogen-containing bases (namely, adenine, guanine, cytosine and thymine), which, upon exposure to a flame or a heat flux, may release ammonia, hence behaving as a blowing agent. 20 bilayers of DNA and chitosan were able to confer self-extinction to the treated fabrics, as assessed with flame spread tests performed in horizontal configuration. At the same time, the combustion kinetics was remarkably reduced [59]. In addition, the deposited coatings showed 40% decrease of the peak of heat release rate in cone calorimetry tests carried out at 35 kW/m<sup>2</sup>.

## Hybrid Organic-Inorganic LbL Assemblies

As mentioned before, the possibility of coupling together multilayers made of nanoparticles (i.e., inorganic layers) with organic molecules in a hybrid layer-by-layer assembly further widened the exploitation of this method for fire retardant purposes. This way, in fact, it is possible to take advantage from the protection given by the char originated by the decomposition of the organic components of the assembly, with the thermal shield effect derived from the ceramic layers.

One of the first attempts of hybrid LbL assemblies dates back to 2012, when **chitosan**, **ammonium polyphosphate** and **silica nanoparticles** positively (i.e., coated with alumina) or negatively charged were built on cotton-polyester blends [52]. In these complex LbL architectures, the fire performances were found to be strictly dependent on the morphology and physical stability of the deposited layers.

Then, LbL assemblies consisting of **amino-functionalized montmorillonite nanoplatelets** and **poly(acrylic acid)** were deposited on cotton [60]. Horizontal flame spread tests revealed a significant decrease of the burning rate of the LbL-treated fabrics with respect to the untreated counterpart; besides, the intumescent character of the deposited assembly was proven by the presence of bubbles (hence of a **swollen charred structure** surrounding the functionalized nanoclay platelets) in the residues after combustion tests.

## RECENT ADVANCES

Multifunctionality in materials science and technology is very important and represents a target, researchers aim to achieve, when new materials systems are conceived and produced. In particular, the LbL approach, thanks to the wide variety of suitable layers, very often offers the opportunity to provide the treated substrates with more than the targeted feature: this is the reason, for which multifunctional LbL architectures, not only possessing flame retardant properties, have been thoroughly investigated.

Very recently, LbL architectures combining **chitosan** and **vitamin B2 sodium phosphate** were designed and applied to **silk fabrics** [61]: this way, it was possible to obtain multifunctional treated fabrics that showed not only enhanced flame retardance, but also antibacterial features. In particular, it was found that limiting oxygen index achieved 28.9 and 32.8%, for the fabrics treated with 5 and 10 bilayers, respectively. Besides, as indicated by vertical flame spread tests, all the LbL-treated fabrics were self-extinguishing. Finally, the treated fabrics showed good antibacterial properties (the inhibition rate was beyond 90%) against either *S. aureus* and *E. coli*.

Polyamide 66 fabrics were LbL-treated with quadlayers made of chitosan, **phytic acid**, **chitosan** and **oxidized sodium alginate** [62]. As assessed by vertical flame spread tests, the fabrics treated with 10 and 15 **quadlayers** were able to prevent melt dripping phenomena. Furthermore, 5 quadlayers were enough for remarkably lowering the peak oh heat release rate (-24% with respect to the untreated fabric), increasing, at the same time, the char residue at the end of the tests.

It was possible to stop the melt dripping phenomena that occur when polyester fabrics are exposed to a flame. For this purpose, **bilayers** consisting of **Octa-ammonium polyhedral oligomeric silsesquioxane** and **sodium montmorillonite clay** were employed [63]. It was found that the ionic strength plays a key role in the growth of the LbL assemblies: in particular, the addition of 0.10 M NaCl to the dipping baths promoted the highest adsorption of each layer during the subsequent deposition steps. The resulting assemblies were more homogeneous and thicker with respect to that obtained without using NaCl: as a consequence, they were able to suppress the melt dripping phenomena during horizontal flame spread tests, slowing down the burning rate, even after 1 h washing carried out at 70°C. Finally, forced-combustion tests performed under 35 kW/m<sup>2</sup> heat flux showed a decrease of the peak of heat release rate by about 50% as compared to the untreated fabrics.

Very recently, **polyethylene terephthalate fabrics** grafted with acrylamide were LbL-treated, depositing assemblies made of **polyethyleneimine** and **oxide sodium alginate**. Then, the treated fabrics were

subjected to cross-linking with hypophosphorous acid [64]. As indicated by **thermogravimetric analyses**, the presence of the cross-linked LbL assembly on the fabric substrate increased its thermal stability, and the final residue as well, hence indicating the char-forming character of the deposited coating. Besides, 15 bilayered assemblies were capable to achieve **self-extinction** in horizontal flame spread tests, preventing at the same time melt dripping phenomena. The LbL-treated fabrics were able to withstand 12 laundering cycles, without losing their fire retardant performances. Finally, as highlighted by **cone calorimetry tests**, the same assemblies deposited on the polyester substrate allowed reducing the peak of heat release rate (-44%) and the total heat release (-29.4%) with respect to the untreated counterpart.

A similar behavior was observed when the same LbL assembly was exploited for conferring flame retardant features to **polyester-cotton blends** [65].

A fully biobased LbL assembly made of chitin derivatives, namely phosphorylated chitin and deacetylated chitin (i.e., chitosan), was exploited for enhancing the flame retardancy of cotton [66]. 20 bilayers were found to provide the cellulosic fabric with self-extinguishing features. 20 bilayers prepared at the high phosphorylated chitin concentration (2 wt%) could extinguish the flame. Micro cone calorimetry tests highlighted lower values of peak of heat release and total heat release with respect to the untreated counterpart.

Another recent example of durable LbL assembly deposited on cotton fabrics was proposed by Pan and co-workers [67], who alternated positively charged **polyethylenimine** (bearing a positive charge) and **hypophosphorous acid-modified chitosan** (bearing a negative charge); the resulting bilayered assembly was cross-linked with **genipin**, i.e., a water-soluble bifunctional crosslinking agent extracted from gardenia fruits. As assessed by thermogravimetric analyses, the deposited assembly showed a char-forming character; in addition, 10 bilayers were sufficient for achieving self-extinction in horizontal flame spread tests. **Micro cone calorimetry** results demonstrated the ability of the deposited LbL coatings to remarkably lower either peak of heat release rate (-73%) or total heat release (-80%), as

compared to the untreated counterparts. Finally, genipin cross-linking provided the fabrics with high washing fastness.

“Green” polyelectrolytes, namely chitosan and phytic acid, were employed for designing durable bilayered architectures on polyamide 66 fabrics; borate was utilized as cross-linker. Despite a slight increase of limiting oxygen index values, the LbL-treated fabrics did not exhibit melt-dripping phenomena in vertical flame spread tests; furthermore, as observed in forced combustion tests, 10 cross-linked bilayers were able to significantly lower the peak of heat release rate (-31%) with respect to the untreated fabric [68].

Chitosan and ammonium polyphosphate were utilized as constituents of intumescent LbL assemblies for enhancing the flame retardant properties of PET fabrics [69]. The resulting coatings showed char-forming properties as revealed by vertical flame spread tests, preventing the melt-dripping phenomena when 10 bilayers were deposited on the fabric substrate. Furthermore, the intumescent character of the proposed LbL architectures was proven by SEM analyses on the residues after flammability tests, which showed the appearance of several microbubbles and a microporous structure.

Very recently, multifunctional LbL-treated cotton fabrics were investigated: in particular, by depositing polyethylenimine/phytic acid layers, as well as silver nanowires, it was possible to obtain conductive networks on the surface of cotton fibers, showing, at the same time, good flame retardant features [70]. 8 bilayers containing 7.5 wt% of silver nanowires not only showed a high electrical conductivity (2416.46 S/m), as well as an outstanding electromagnetic interference shielding effectiveness (32.98 dB), but were also capable to confer self-extinction to the cellulosic substrate, significantly reducing the peak of heat release rate (by about 59% with respect to the untreated fabric). Furthermore, the multifunctional features were maintained even during bending, washing and sandpaper abrasion tests.

Another recent example of multifunctionality refers to the LbL deposition of a superhydrophobic and flame-retardant assembly made of branched poly(ethylenimine), ammonium polyphosphate and fluorinated

silica@polydimethylsiloxane composite, using a dipping method, on cotton [71]. The resulting treated fabrics showed superhydrophobic surfaces (water contact angle: 158°), with outstanding self-cleaning and antifouling features. Furthermore, as assessed by vertical flame spread tests, the treated fabrics reached self-extinction, showing, at the same time, the formation of a consistent and coherent char, due to synergistic effect occurring in between ammonium polyphosphate and the fluorinated silica@polydimethylsiloxane composite. Finally, micro cone calorimetry tests showed a strong reduction of both peak of heat release rate and total heat release as compared to the untreated cellulosic substrate.

Assemblies consisting of layers of polyethyleneimine embedding silica nanoparticles and phytic acid were recently deposited on cotton, by means of a layer by layer technique [72]. It was found that 7 bilayers were enough for remarkably increasing the limiting oxygen index of cotton (from 18 to 33.7%) and for achieving self-extinction in vertical flame spread tests. In addition, forced combustion tests highlighted a significant reduction of peak of heat release rate (-75%) and total heat release (-52%) of the LbL-treated fabrics with respect to untreated cotton. Finally, the assemblies deposited on the cellulosic substrate did not change the “hand,” i.e., the mechanical behavior of the fabric.

## CONCLUSION AND PERSPECTIVES

It is undoubtable that LbL represents a valued approach non only for the nano-structuration of several types of surfaces, but also for improving the flame retardant behavior of the treated substrates.

Among the pros of this method, the “unlimited” freedom in the design of the LbL architecture seems to be the most important. As a result, the layer-by-layer assemblies can provide different flame retardant outcomes, listed as follows:

- **Thermal shielding**, when the assemblies are based on the use of nanoparticles

- **Intumescence**, when some intumescent constituents are selected as layers for building the coating structure
- **Thermal shielding** and **intumescence**, when hybrid organic-inorganic assemblies are employed.

As a consequence, it is quite common that, on the basis of the structure and composition of the assemblies, multiple flame retardant mechanisms may occur simultaneously, even sometimes exploiting **synergistic effects**.

This **surface engineered technique** shows the potential to efficiently replace the conventional flame retardant additives, especially those showing suspected/assessed toxicity and high environmental impact.

Conversely, at present, the LbL approach is still facing some important limitations that are somehow restrain its potential use, particularly referring to an industrial scale development.

First of all, this technique shows some limitations concerning its **scalability**, from lab-scale to at least semi-pilot/pilot scale. In fact, the standard LbL deposition (i.e., exploiting a dipping procedure) is monotonous and has to be carried out with an extensive manual procedure: these issue may limit its direct scalability to industrial applications. On the other hand, spray-assisted LbL seems to be more suitable at an industrial scale than dipping: in fact, spraying is faster and avoids cross-contamination of the solutions/suspensions baths; as a matter of fact, some attempts to scale spray-assisted methods at a pre-industrial scale have been already done [73].

Another strong limitation, the LbL approach is experiencing, refers to the **weatherability/durability** of the deposited architectures. It is clear that water-borne layers, if not properly covalently linked, cannot resist to washing cycles, the fabrics usually have to undergo during their use: as a consequence, the fire performances provided by the LbL architectures are almost lost, because of the removal of the layers. One of the possible solutions, already proposed at a lab-scale, is to functionalize the layer constituents with reactive groups that, upon heating or exposure to **UV-radiation** [45, 74], link together the assembly, hence ensuring the required washing fastness. Durability also refers to the stability of the assembly, which may be exposed to physical friction and bacterial erosion, among a

few to mention: again, in these conditions, the possibility of designing strong architectures where every layer is covalently bonded to each other and to the fabric substrate, greatly enhances the weatherability of the LbL assemblies. In some cases, as in humid or dusty environments, the design of FR superhydrophobic architectures may fix the durability problems.

Finally, another possible limitation of the LbL method refers to the evidence of bridging fibers during the LbL deposition: as a consequence, the comfort of the fabric may worsen, as it becomes stiffer and loses its “hand” (i.e. **soft touch**). This issue can be quite easily solved by utilizing ultrasonication during the rinsing step [75].

In conclusion, the potentiality of the LbL method for designing new and cost-effective flame retardant architectures, together with the chance of employing low environmental impact constituents for the layers, may justify its fast and continuous expansion over different substrates, hence probably resulting in FR layer-by-layer solutions “ready to the market” within the forecoming years.

Besides, though there are still several fabrication procedures that have not been integrated with the layer-by-layer process, it seems reasonable that their integration will bring to specific multilayer features, or accelerated deposition processes. Finally, some work still has to be carried out for an in-depth characterization of the different assembly processes in situ, as well as for the setup of suitable and reliable methods for the prediction of the properties and performances of LbL architectures, directly on the basis of the chemical structure of the selected layers, on the deposition conditions, and on assembly techniques: in this context, computational methods could be very helpful.

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## BIOGRAPHICAL SKETCH

*Giulio Malucelli*

**Affiliation:** Politecnico di Torino, Dept. of Applied Science and Technology, Viale Teresa Michel 5, 15121 Alessandria, Italy.

**Date of Birth:** 6 November 1967.

**Education:** M. Sci. in Chemical Engineering (1992), PhD in Chemistry (1996).

**Address:** Viale Teresa Michel 5, 15121 Alessandria (Italy).

**Research and Professional Experience:** Full Professor of Materials Science and Technology.

**Professional Appointments:**

- Founder of the Italian Macromolecular Association and Member (from 2011 to 2016) of the Steering Committee of the Italian Macromolecular Association
- Member (from 2013 to 2016) of the Steering Committee “Sustainable flame retardancy for textiles and related materials based on nanoparticles substituting conventional chemicals,” FLARETEX (MP1105).

**Honors:****Publications Last Four Years (on peer-reviewed journals):**

1. Malucelli, Giulio Marco Barbalini. UV-curable acrylic coatings containing biomacromolecules: A new fire retardant strategy for ethylene-vinyl acetate copolymers. *Progress in Organic Coatings*, vol. 127, p. 330-337, ISSN: 0300-9440, doi: 10.1016/j.porgcoat.2018.11.039.
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