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Tunable thermal and flame response of phosphonated oligoallylamines layer by layer assemblies on cotton

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ABSTRACT

In the present paper we have demonstrated how the change of the layer by layer deposition parameters can influence the final properties of cotton fabrics in terms of coating morphology, thermal stability and flammability. To this aim, novel synthetized oligoallylamines and phosphonated oligoallylamines have been assembled on the surface of cotton exploiting different molecular weights and pH conditions. Low molecular weights have yielded an incomplete "island growth" coating while high molecular weight resulted in a homogeneous coating which thickness was controlled by the adopted pH. Both low and high molecular weight assemblies induced a reduction of the cellulose decomposition temperatures that was, conversely, delayed by coatings assembled at pH = 10. All assemblies were able to improve cotton flammability by suppressing the afterglow phenomenon; the best results in terms of flame spread and final residue have been achieved by high molecular weight assemblies.

1. Introduction

During the last years, the layer by layer (LbL) technique has been presented and studied as a versatile surface engineering tool for conferring thermal and fire protection to various kinds of substrates. (Alongi, Carosio, & Malucelli, 2014; Carosio, Alongi, Frache, Malucelli, & Camino, 2012; Carosio, Di Blasio, Alongi, & Malucelli, 2013; Kim, Davis, Amanda, Cain, & Grunlan, 2011; Laachachi, Ball, Apaydin, Toniazzo, & Ruch, 2011).

Among all substrates understudy, cotton represents one of the most important for both its wide distribution and need for protection. Moreover, cotton fibre hydrophilicity and natural surface roughness can certainly promote and favour the formation of a homogenous coating during LbL assembly. This technique, in which fundamentals can be dated back to 1966, has been heavily exploited only after the reinvention by the group of Decher in early 90s (Decher & Hong, 1991; Iler, 1966).

One of the strong key parameters relies in the simplicity of the deposition that is based on the alternate adsorption of chemical species on the surface due to specific interactions occurring between selected reagents. The most common and, at the same time, most exploited interactions are certainly the electrostatic interactions occurring between oppositely charged polyelectrolytes or nanoparticles. (Bernt, Kurihara, & Kunitake, 1992; Ladam et al., 2000.) If compared to more traditional surface modification techniques, the LbL offers several advantages such as the easy incorporation of multifunctional materials (with the possibility of imparting different surface properties with one coating), a process that takes place under ambient conditions (room temperature, atmospheric pressure) and intrinsic environmentally friendly characteristics (the most common solvent employed is water, the solutions/dispersions concentrations are below 1 wt%, it is possible to recycle suspension baths after use).

Another key point of the above technique, that makes this approach even more attractive, is represented by the possibility of fine tuning the physical/chemical characteristics of the deposited coating by adjusting and controlling the deposition parameters such as chemistry of used polyelectrolyte (Mermut & Barrett, 2003), and thus their molecular weight (Sui, Salloum, & Schlenoff, 2003), temperature (Chang, Kong, Wang, Wang, & Shen, 2008; Tan, McMurdo, Pan, & Van Patten, 2003), counterions (Zhang & Ruhe, 2003), ionic strength (McAloney, Sinyor, Dudnik, & Goh, 2001), and pH (Shiratori & Rubner, 2000). However, while the above parameters have been widely studied for most of the application fields,

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there are few studies dealing with the effect of the deposition parameters, mainly pH, on the achieved fire protection performance. As an example, Li et al. have shown the pH effect on the fire performance of branched polyethylenimine/clay assemblies on cotton (Li, Schulz, & Grunlan, 2009; Li et al., 2010). By changing the pH, it was possible to control both the coating thickness and composition, and thus change the resulting properties of coatings; fire testing results demonstrated that the coatings with higher clay loading were able to deliver the best performances. pH has been also adopted to change the coating composition of LbL assemblies made of chitosan and phytic acid (PA); the coatings deposited at pH = 6 were thicker and had 48 wt% PA content, while pH = 4 yielded the thinnest deposition with 66 wt% PA. (Laufer, Kirkland, Morgan, & Grunlan, 2012). Only this latter formulation was capable of completely extinguishing the flame in vertical flame test as a consequence of the high phosphorous content provided by PA.

Working on another controlling parameter, Fang et al. studied the effect of polyelectrolyte/nanoparticle concentrations on the layer by layer assembly of protective coatings on ramie fabrics. (Zhang, Yan, Wang, & Fang, 2013). They showed that, by increasing the concentration of the adopted solution or suspension, a better surface coverage and thus a better fire protection can be achieved.

It is evident that the study of the correlation between the deposition parameters and the achieved fire protection represents an important research field capable of greatly improving the performances of a selected LbL architecture with small modifications of the deposition process. However, as mentioned above, this particular research field has not been thoroughly exploited.

For this reason, in the present paper we have thoroughly investigated the effect of different molecular weights and pH conditions on LbL assemblies consisting of oligoallylamines and phosphonated oligo-allylamines deposited on cotton fabrics. Indeed, these aspects may strongly affect the resulting properties of cotton fabrics in terms of thermal and fire stability.

In our previous work, we have optimized the synthesis of these two oligomers that, when assembled through LbL, have exhibited a high thermal stability in air, encouraging their application as coating on a substrate (Negrell-Guirao, Carosio, Boutevin, Cottet, & Loubat, 2013). Thus, the coating concept is here transferred to cotton fabrics in an effort to improve its thermal and fire protection, assessing at the same time the effect of different molecular weights and pH. The morphology of the treated fabrics has been imaged by scanning electron microscopy (SEM) and correlated to the adopted deposition parameters. Then, the thermal stability in nitrogen and air as well as the resistance to a direct flame application has been assessed by thermogravimetric analyses and vertical flame tests, respectively. Finally, the morphologies of the residues collected after vertical flame tests have been correlated to the adopted deposition parameters and the achieved fire protection performances.

2. Materials and methods

2.1. Materials

Cotton (COT, 200 g/m^2) was purchased from Fratelli Ballesio S.r.l. (Torino, Italy). Prior to the LbL deposition, cotton fabrics were washed with water and Marseille soap, ethanol and then diethyl ether. After that, fabrics were dried in an oven at 70 °C for 1 h.

Allylamine, 2,2′-azobis(2-methylpropionamidine)dihydrochloride, formaldehyde, phosphonic acid, NaOH and HCl (35%) were supplied by Sigma–Aldrich or Acros (all reagent grades) and used without further purification.

2.2. Synthesis of poly(allylamine) hydrochloride and phosphonated poly(allylamine)

As shown in a previous publication, (Negrell-Guirao et al., 2013) phosphonate containing-poly(allylamine) oligomers, named PAA-P, were synthesized according to a two-step reaction. In the first step, the radical polymerization of allylamine under its cationic form generated oligomers of poly(allylamine) under their cationic form, named PAA-HCl. The second step consists in the functionalization into phosphonic acid groups through the Moedritzer–Irani reaction to obtain the corresponding PAA-P (Oie, Sudo, & Endo, 2011).

In order to evaluate the effect of the molecular weight on the LBL properties, two oligomers were synthesized with M_n of 4500 g/mol and 20,000 g/mol. These oligomers have been coded LW and HW for low and high molecular weight, respectively. For assessing the purity and the molecular weight values of the oligomers, both ^{1}H and ^{31}P nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC) measurements were performed (see Figs. S1A for NMR and S1B for SEC in supporting information).

Synthetized PAA-HCL and PAA-P, LM or HM, were used to prepare 0.1 wt% solution; the pH of PAA-P HM solution was adjusted to 10 with 1 M NaOH solution.

2.3. LbL deposition

In order to activate the cotton surface and prepare it for the further LbL deposition, the very first layer was grown by dipping for 20 min into BPEI solution followed by a washing step with water to extract the residues of counterions. After this first step, the substrate was alternately immersed into negatively (phosphonated oligomers) and positively (oligoallylamines) charged solutions; after each immersion step, the fabric was washed with deionized water to remove excess polyelectrolytes. As the first couple of layers are the most important for the uniformity and stability of the coating, the immersion period for these layers was 10 min, followed by 5 min for subsequent layers. The process was repeated until samples with 5, and 10 bilayers (BL) were built for each system as schematized in Fig. S2. In the followings, assemblies performed will be denoted as: LM for low molecular weight oligomers, HM for high molecular weight oligomers and HM pH10 for high molecular weight oligomers with pH of PAA-P corrected to 10. Each of the above code (i.e. LM, HM or HM pH10) will be preceded by the number of BL deposited.

2.4. Characterization techniques

The details of NMR and SEC measurements employed to characterize the synthetized oligomers are reported in the supporting information file (Fig. S1).

The surface morphology of the LbL-treated fabrics was studied using a LEO-1450VP Scanning Electron Microscope (beam voltage: 5 kV), equipped with an X-ray probe (INCA Energy Oxford, Cu Kα X-ray source, k = 1.540562 Å), which was used to perform elemental analysis. Fabric pieces (0.5 cm × 0.5 cm) were cut and fixed to conductive adhesive tapes and gold-metallized.

The thermal stability of the fabrics was evaluated by thermogravimetric (TG) analyses from 50 to 800 °C with a heating rate of 10 °C/min, both in nitrogen and in air (60 mL/min). To this aim, a TAQ500 thermogravimetric balance was used, placing the samples in open alumina pans (ca. 10 mg). The experimental error was 0.5% on the weight and 1 °C on the temperature. TGA plots showed afterwards are related to the 150–650 °C range that is considered the most representative for cotton thermal and thermoxidative degradation.

The flame retardancy properties of the prepared samples were measured using a vertical flame spread test, applying a methane flame for 5 s at the bottom of a fabric specimen (50 mm × 100 mm) and repeating the test 3 times for each formulation in order to get reproducible data; burning time, afterglow time and the final residue were measured.

3. Results and discussion

3.1. Coating morphology of LbL coatings on cotton fibres

Scanning electron microscopy (SEM) has been adopted in order to assess the change in cotton surface morphology after the LbL deposition. Fig. S3 reports two SEM micrographs of untreated cotton at different magnifications. Untreated cotton presents a rough surface morphology typical of a natural fibre; such surface roughness, along with cotton hydrophilicity, represents an important parameter for the deposition and growth of a LbL coating. SEM micrographs of cotton after the LbL deposition are reported in Fig. 1.

As it can be observed from Fig. 1(a) and (b), the deposition of oligomers at low molecular weight is not capable of yielding a homogeneous and continuous coating on the cotton fibres. Indeed, both 5 and 10 BL LW show the formation of coating islands easily distinguished from the cotton surface due to their smooth surface. The "island growth", by which the coating starts growing from separated islands that gradually coalesce, is commonly found in the LbL assemblies and it is generally confined in the first deposition steps

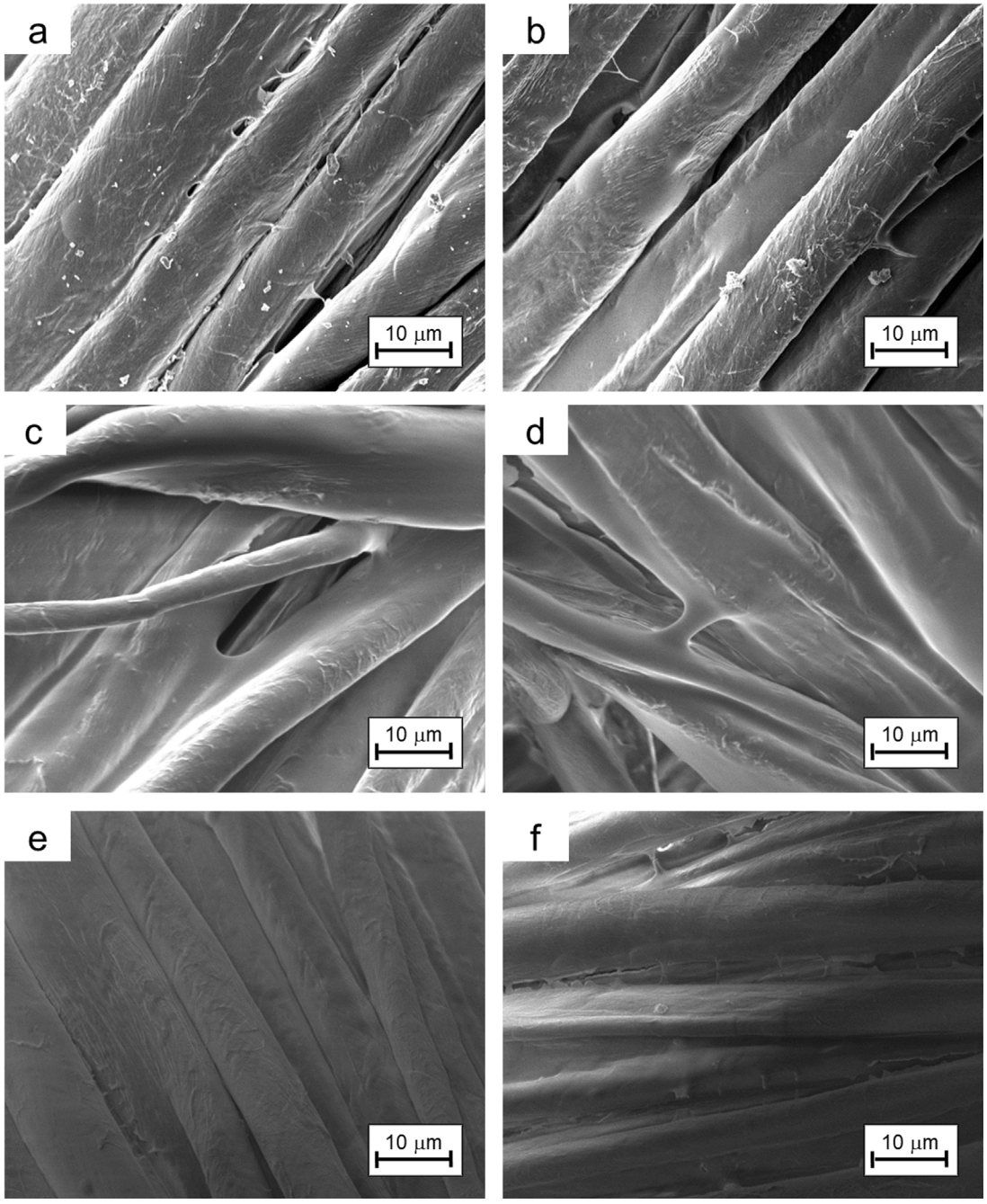

Fig. 1. SEM micrographs of cotton treated by LbL: 5 (a) and 10 (b) BL LM, 5 (c) and 10 (d) BL HM, 5 (e) and 10 (f) BL HM pH10.

(Schmitt et al., 1993). In this particular case, the average molecular weight, in combination with the adopted deposition times, is not high enough in order to guarantee the coalescence of the islands; indeed, the deposition of 10 BL can only improve the surface coverage achieved with 5 BL without reaching the formation of a continuous coating. By increasing the average molecular weight, a better surface coverage can be achieved as pointed out in Fig. 1(c) and (d); indeed, 5 BL HW shows the formation of a coherent and continuous coating capable of randomly joining together adjacent fibres. By increasing the number of BL to 10 the coating grows thicker and the number of joined fibres increases. The increased surface coverage and coating thickness achieved by increasing the molecular weight of the adopted polyelectrolytes certainly represents a positive result; however, the formation of coating bridges in between cotton fibres is not favourable as it might result in a change in the mechanical properties of the fabric. This phenomenon can be limited by adjusting the pH of the negative suspension, and subsequently changing the charge density of the polyelectrolyte; without any change of pH, the phosphonate groups of PAA-P are poorly dissociated, thus resulting in a low charge density on the polymer chain that subsequently adsorbs on the surface in a random coiled configuration, greatly increasing the coating thickness at each deposition step. Such behaviour is well known and has already been reported for other polyelectrolytes (Shiratori & Rubner, 2000; Yamada and Shiratori, 2000). By increasing the pH value to 10, the charge density may be increased so that the PAA-P chains may adsorb in a flat conformation, thus resulting in a thinner coating. As reported in Fig. 1(e) and (f), the depositions performed with the PAA-P solution at pH 10 yielded a thin and continuous coating, clearly recognizable by the change in the surface roughness of cotton fibres (*compare* Fig. S3 with Fig. 1(e) and (f)), with a limited, if not absent, joining of adjacent fibres.

Table 1
Thermogravimetric data of untreated and LbL-treated cotton fabrics in nitrogen.

Sample	$T_{onset\ 10\%}$ [°C]	T_{max}[a] [°C]	Residue at 650 °C [%]
COT	317	356	13
5 BL LM	292	314	20
10 BL LM	298	318	17
5 BL HM	306	326	20
10 BL HM	309	325	22
5 BL HM pH10	330	350	14
10 BL HM pH10	332	346	17

[a] From derivative TG curves.

3.2. Thermal stability of LbL-treated cotton fabrics

The thermal and thermo-oxidative stability of untreated and LbL-treated cotton has been assessed by thermogravimetric analyses in nitrogen and air, respectively. Fig. 2 reports TG and dTG curves in nitrogen of untreated cotton in comparison with cotton treated by 10 BL of each different formulation understudy; Table 1 reports thermogravimetric data of untreated and LbL-treated cotton fabrics in nitrogen.

As well described in the literature, the cotton thermal degradation proceeds by one step, as reported in Fig. 3, that is the result of two alternative pathways: the depolymerization of the glycosyl units to volatile products containing levoglucosan and the decomposition of such units to char that yields the final residue (Alongi, Camino, & Malucelli, 2013).

The deposition of the LbL coating containing both low and high molecular weight oligomers is responsible of a reduction of the cellulose decomposition temperatures, as reported by $T_{onset\ 10\%}$ values in Table 1 and depicted in Fig. 2. This behaviour can be ascribed

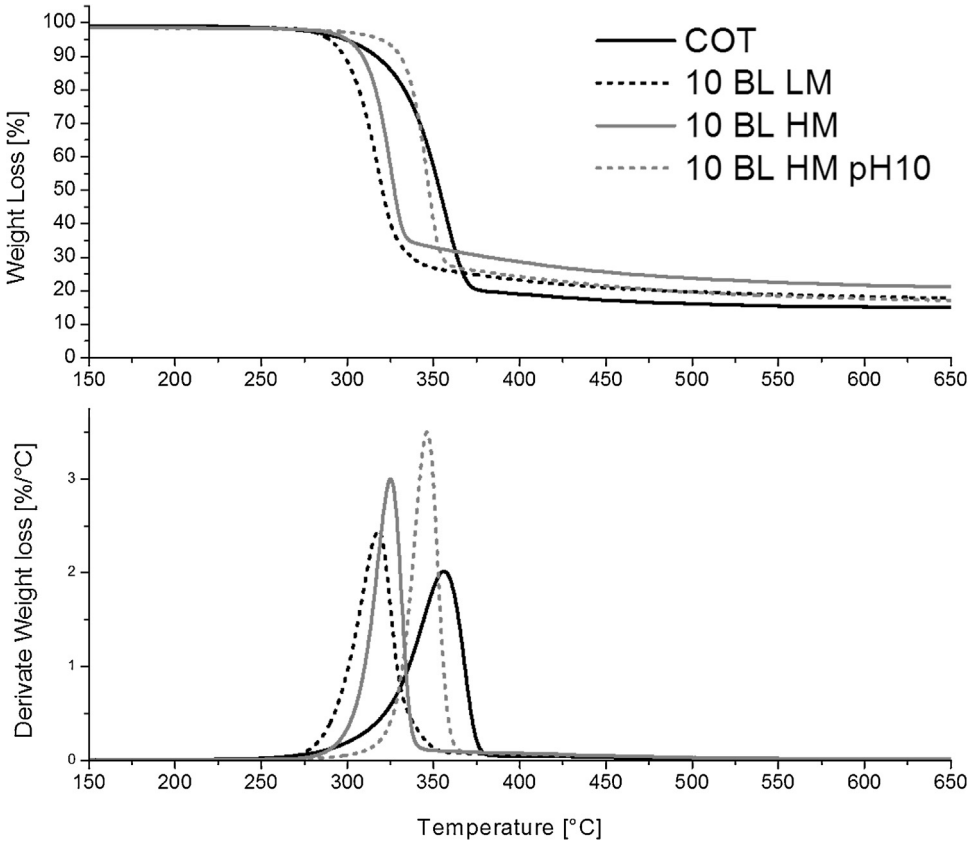

Fig. 2. TG and dTG plots of untreated and LbL-treated cotton in nitrogen.

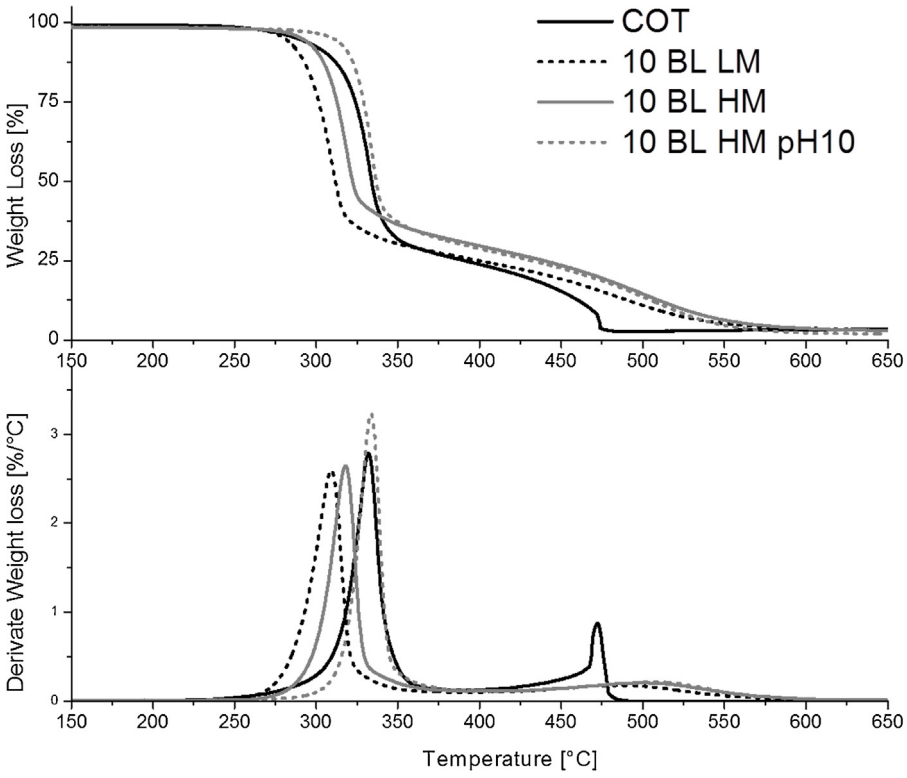

Fig. 3. TG and dTG plots of untreated and LbL-treated cotton in air.

to the phosphonate groups of the PAA-P polyelectrolyte that can induce the dehydration reaction of cellulose towards the formation of an aromatic char (Price, Horrocks, Akalin, & Faroq, 1997). Such process is also supported by a physical mechanism exerted by the coating that is able to evolve into a thermally stable structure that is capable of acting as a barrier limiting heat transfer to the substrate, thus enhancing its char-forming feature. As a consequence of these combined mechanisms, both low and high molecular weight assemblies yield final residues higher than that left by untreated cotton (*see* Table 1). It is worth noticing that the final residue of 5 BL LW is higher than 10 BL LW; this odd behaviour can be ascribed to the poor surface coverage and homogeneity of the coating, already observed by SEM.

Surprisingly, when cotton is treated with the HM pH10 formulation, a 15 °C delay in thermal degradation is observed. Such difference with the previous assemblies can be ascribed to the complete dissociation of PAA-P phosphonate groups, which acid H cannot catalyze the cotton dehydration reaction anymore; as a consequence, the coating physical barrier postpones the cotton thermal degradation.

Fig. 3 reports TG and dTG plots of untreated and LbL-treated cotton in air; the corresponding thermogravimetric data are reported in Table 2.

The thermal-oxidation of neat cotton occurs by two steps: the first is found in between 300 and 400 °C and involves the formation of both volatile products and aliphatic char while the second takes place in between 400 and 600° and it is related to the further oxidation of the formerly produced aliphatic char with CO and CO_2 production. As far as the treated fabrics are concerned, no changes can be detected in the cotton degradation mechanism that still proceeds in two steps. Once again, LM and HM show a sensitization of cotton in the first degradation step; such anticipation is more pronounced for LM samples, as reported by $T_{onset\ 10\%}$ temperatures in Table 2. On the other hand, for HM pH10 samples a delay in the thermo-oxidative degradation is observed. After this first step, both HM and HM pH10 samples are capable of producing a char residue with increased thermo-oxidative stability with respect to untreated cotton; such behaviour can be observed from TG curves that remain at higher weight percentage in the 400–550 °C range (cotton residue at 500 °C is <2% while is around 18% for HM and HM pH10 samples). Moreover, the second degradation step is consistently slowed down for all LbL-treated samples, as clearly demonstrated by dTG curves that are flattened (Fig. 3).

3.3. Flammability of LbL-treated cotton fabrics

Being among the first item to be ignited in a fire, it is of great important to study the reaction of the treated fabrics to a direct flame application. For this reason, untreated and treated fabrics have been subjected to flammability test in vertical configuration. Fig. 4 reports some snapshots taken at different fixed times during the tests of untreated and LbL-treated fabrics and Table 3 collects the data gathered during each test.

Table 2
Thermogravimetric data of untreated and LbL-treated cotton fabrics in air.

Sample	$T_{onset\ 10\%}$ [°C]	T_{max1}[a] [°C]	T_{max2}[a] [°C]	Residue at 650 °C [%]
COT	307	331	472	<2.0
5 BL LM	285	307	490	<2.0
10 BL LM	290	309	493	<2.0
5 BL HM	298	315	496	<2.0
10 BL HM	301	318	502	<2.0
5 BL HM pH10	320	335	510	<2.0
10 BL HM pH10	321	335	510	<2.0

[a] From derivative TG curves.

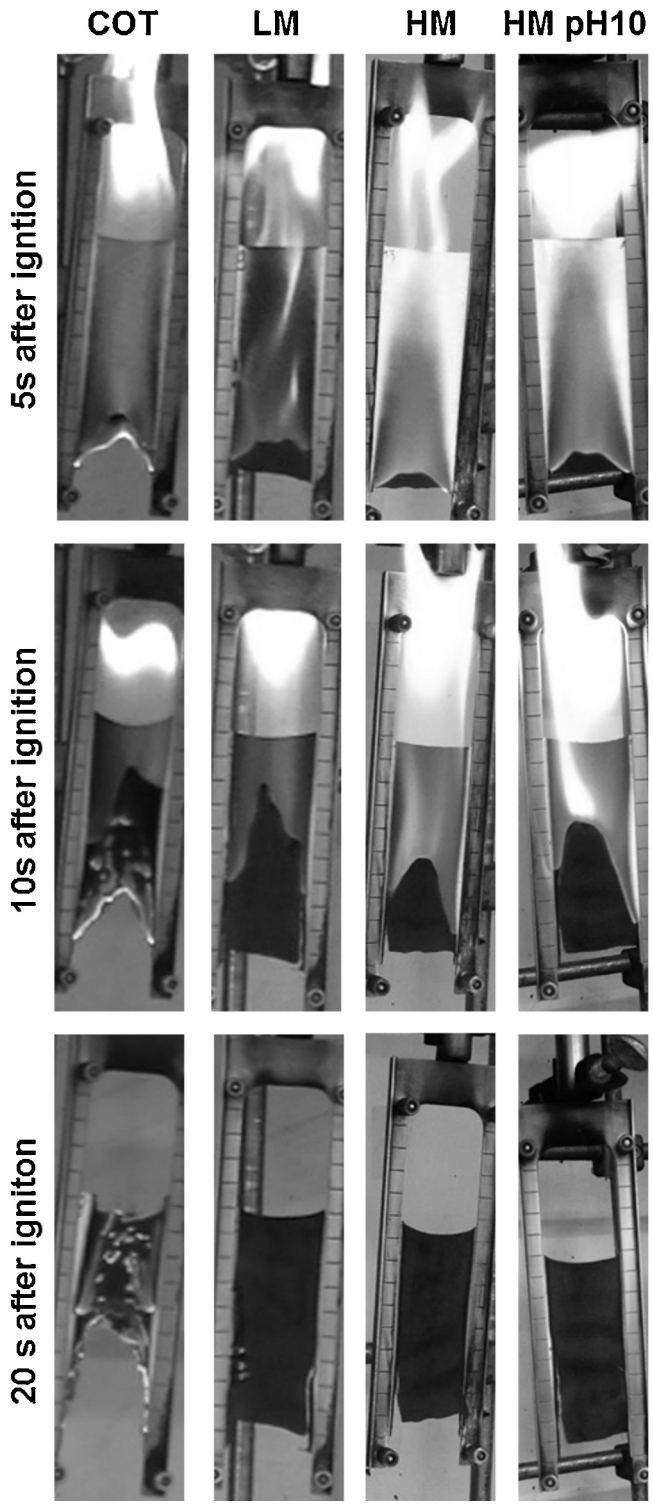

Fig. 4. Vertical flame test snapshots of untreated and LbL-treated cotton taken at different times after ignition.

Upon flame application pure cotton immediately ignites and burns with a vigorous flame that quickly spreads to the entire fabric in less than 5 s, as reported in Fig. 4. The flame eventually extinguishes giving room to the afterglow; this phenomenon, visually recognizable as a red glowing on the fabric (*see* Fig. 4 cotton snapshot at 20 s), is characterized by the flameless combustion of the remaining charred residue and ceases when the residue is completely consumed (the final residue of untreated cotton is 0%).

Table 3
Flammability data of untreated and treated cotton fabrics.

Sample	Total burning time [s]	Afterglow time [s]	Residue [%]
COT	16	43	–
5 BL LM	18	–	11
10 BL LM	17	–	13
5 BL HM	22	–	16
10 BL HM	19	–	19
5 BL HM pH10	23	–	10
10 BL HM pH10	19	–	12

Although the flame has extinguished, the afterglow still represents a safety threat as it can spread the fire to other ignitable materials due to the high temperatures reached by the incandescent residue.

When cotton is LbL-treated, a general improvement in the flame resistance of cotton can be easily detected; indeed, all treated fabrics were able to increase the burning times, suppress the afterglow phenomenon and leave a coherent residue at the end of the test, as reported in Fig. 4 and Table 3.

Among the LbL-treated fabrics, it is worth noticing that the best performances have been achieved by the assemblies that were capable of homogenously cover the cotton fabrics. Indeed, even though LM samples clearly improved the performances of cotton, they were not able to match those of HM and HM pH10 samples. In details, only for these latter the initial flame spread after ignition is slowed down, as reported in Fig. 4; indeed, as demonstrated by snapshots taken 5 s after ignition, both HM and HM pH10 samples still present portions of the fabric not reached by the flame that, conversely, had spread to the entire surface of cotton and LM samples. The final residue reaches the highest values for HM assemblies (16 and 19% in weight for 5 and 10 BL, respectively); this can be ascribed to the thick coating achieved by these assemblies, as demonstrated by SEM observation reported in Fig. 1.

The 10 BLs residue of each deposited LbL assembly have been imaged by SEM; collected micrographs are reported in Fig. 5.

As observable from Fig. 5(a), (d) and (g), all treated fabrics were able to leave a coherent residue still having the original fabric texture. By increasing SEM magnification, different residue morphologies are revealed; indeed, for both LM and HM samples, it is possible to detect the formation of intumescent-like micro bubbles whereas no bubbles can be found in HM pH10 samples. Such particular difference can be ascribed to the coating thicknesses: if the deposited LbL architecture was able to reach a specific thickness, the volatile products released from the substrate, the release of ammonia from PAA-HCl in combination with PAA-P charring ability can result in the formation of blown charred structures made of phosphorous, carbon and oxygen elements. As far as LM and HM samples are concerned, the effect of the different molecular weight is observed on the size and surface density of the bubbles: indeed, as reported in Fig. 5, the HM coating yielded an increased number of blown structures with respect to the LM one probably because of the poor surface coverage of this latter. Moreover, the bubbles produced from HM appear to be the biggest one (*compare* Fig. 5(b) and (c) with (e) and (f)); the micrograph reported in Fig. 5 clearly shows the hollow structure of the intumescence bubbles.

Notwithstanding the absence of blown structures, HM pH10 coatings were capable of evolving into a thin charred coating that protects the fabric during combustion maintaining cotton original texture and fibres mostly undamaged; by increasing the magnification it is possible to reveal the real structure of the fibres that are hollow as reported in Fig. 5(h).

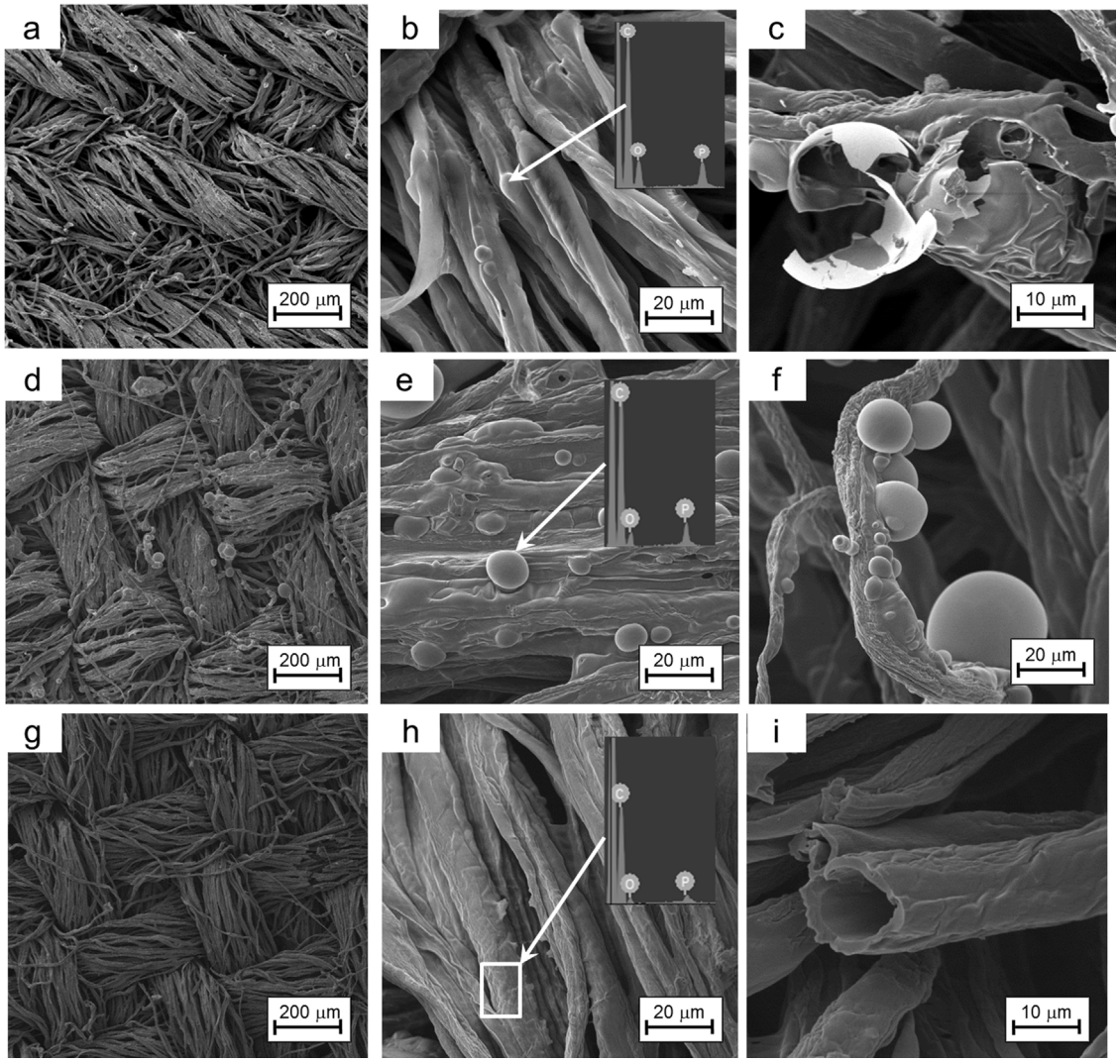

Fig. 5. SEM micrographs at different magnifications and elemental analyses of residues collected after flammability tests: 10 BL LM (a–c), 10 BL HM (d–f) and 10 BL HM pH 10 (g–i).

4. Conclusions

In the present paper the layer by layer assembly of novel synthetized oligoallylamines and phosphonated oligo-allylamines has been employed for the surface protection of cotton fibres.

The effects of different molecular weights and pH conditions on the coating morphology as well as on cotton thermal and thermo-oxidative stability and flammability properties have been thoroughly investigated. By increasing the molecular weight of the adopted oligomers, a homogeneous thick coating was achieved, even at low BL numbers; the further change of pH greatly reduced the coating thickness, due to the increased charge density of phosphonated oligoallylamines. From the thermal and thermo-oxidative stability point of view, both low and high molecular weight induced a reduction of the cellulose decomposition temperatures while, surprisingly, coatings assembled at pH 10 induced a delay in cotton degradation. Flammability test showed that all assemblies suppressed the afterglow phenomenon while the best results in terms of flame spread have been achieved by both HM and HM pH10 assemblies.

In conclusion, we have demonstrate how, once the chemistry of the layer by layer assembly has been selected, the change of deposition parameters can greatly affect the final properties achieved in terms of coating morphology, thermal and thermo-oxidative and flammability behaviour. Such study, together with the environmentally friendly nature of the process and the relatively few bilayers adopted, represents an interesting starting point worthy to be further developed.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.06.066.

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