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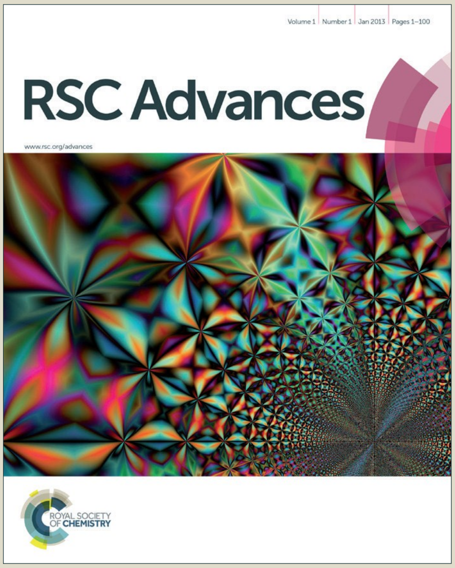

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Few durable layers suppress cotton combustion thanks to the joint combination of Layer by Layer assembly and UV-curing

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Abstract

In the last five years, Layer by Layer (LbL) assembly has proven to be one of the most innovative solutions for conferring flame retardancy to fabrics. In spite of this, two main issues for the breakthrough of this approach at an industrial scale are still unsolved: namely, the use of few efficient layers characterized by washing durability. In this context, the present manuscript shows that both these limits can be overcome by coupling the LbL with the UV-curing processes in a joint action. In detail, 3 bi-layers (BL) consisting of an anionic UV-curable aliphatic acrylic polyurethane latex doped with a phosphorus-based flame retardant (namely, ammonium polyphosphate, APP) and chitosan have been initially deposited on cotton fabrics by dipping. Subsequently, this assembly has been exposed to UV radiation, thus resulting in a thin coating in which APP is in intimate contact with chitosan within a UV-cured network. This system has proven to be an efficient flame retardant system with exceptional durability features. Indeed, cotton self-extinguishment in horizontal flame spread tests has been achieved, even after washing in water at 65°C for 1h. Furthermore, this coating managed to withstand the attack of a 1M solution of acetic acid or ammonia for 1h, without losing its original structure. Indeed, no visible signs of coating hydrolysis or somewhat degradation phenomena have been observed by scanning electron microscopy.

Keywords: cotton; Layer by Layer assembly; UV-curing; flame retardancy; durability.

1. Introduction

Cotton flammability is one of the most relevant safety related issues of this century. As recently reviewed by our research group, huge academic and industrial efforts have been carried out through years in order to solve such problem and find innovative solutions [1, 2]. In the continuous seek of new flame retardant systems for suppressing cotton combustion, the Layer by Layer assembly appears to be the most innovative and promising approach, attracting the interest of several research groups, such as that of Grunlan [3-14], who firstly proposed the use of LbL for flame retardancy purposes, of Huang [15-17] and our group [18-25]. The reasons have to be searched in the great simplicity and versatility of this technique that relies on electrostatic attractions occurring between polyelectrolytes and nanoparticles in aqueous media for the multi-step deposition of nanostructured coatings. The composition and structure of LbL coatings can be easily tuned allowing to target specific flame retardant mechanism such as thermally shielding coatings mainly made of nanoparticles or intumescing coatings that easily incorporate the classical components of an intumescent formulation. Through years of research, the performances of these systems have been greatly improved, imparting self-extinguishing behaviour to many substrates such as natural and synthetic fabrics, polyurethane foams and thin plastic films. Despite this, there are two main issues that are currently holding the exploitation of this technique at an industrial scale: namely, the use of a low number of layers to deposit and the washing durability of such treatments. Indeed, nowadays most of the papers already published refer to a minimum number of 5-10 bi-layers and none of these systems has proven to be durable to washing or chemically stable when treated with an acid or a base. Very recently, we have demonstrated that it is possible to reduce the number of deposited bi-layers down to 2 by using a bio-based intumescent flame retardant system that can guarantee cotton self-extinguishing [19]. On the other hand, a first attempt for ensuring the chemical stability (and thus durability) of LbL coatings has been already carried out in our laboratories, exploiting UV-curing processes for enhancing the flame retardancy of polycarbonate films, reducing its dangerous dripping [26]. The experience acquired in the previous two studies has intensely motivated us to pursue the efficient combination of LbL assembly and UV-curing processes (Figure 1).

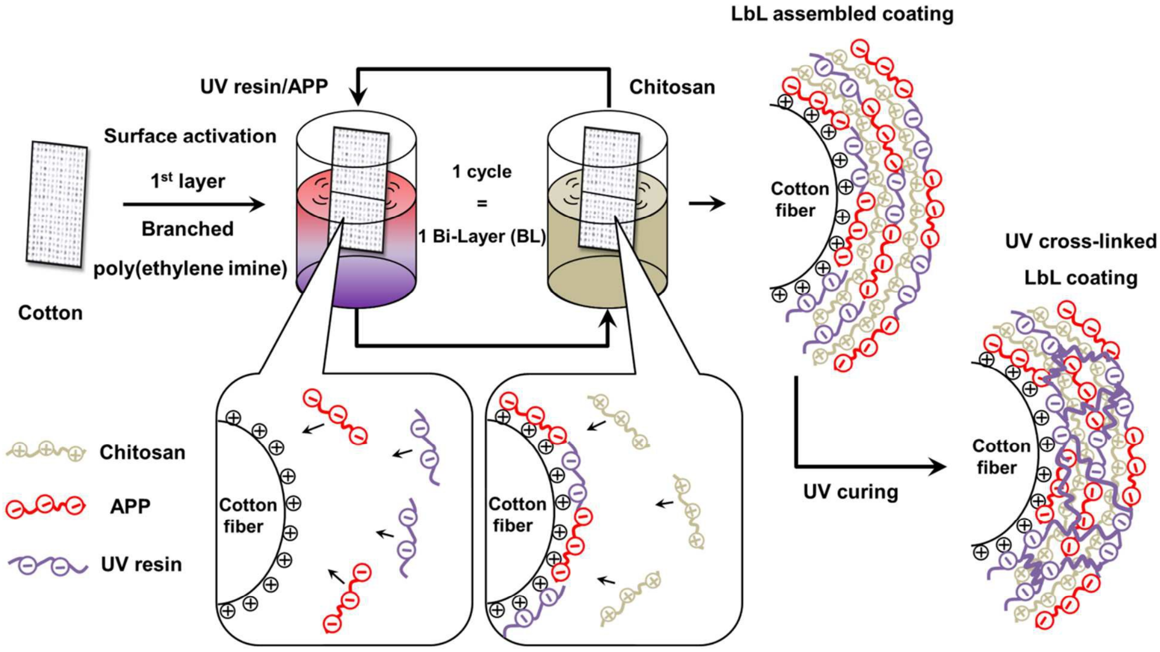

Figure 1. Schematic representation of the deposited LbL assembly. Cotton fabrics are pre-activated by a branched poly(ethylene imine) and then alternatively dipped in the UV-curable resin +APP emulsion (negative) and chitosan solution (positive).

The process was repeated in order to deposit 3BL.

In this contest the UV-curing technology represents one of the fastest and most efficient methods available and able to generate highly cross-linked 3D polymer networks; furthermore, it also possess green aspects such as the reduced energy consumption and the absence of volatile organic compounds emissions. In the opinion of the Authors, the joint action of these two technologies can be highly performing for reaching the multipurpose of a durable LbL coating that suppresses cotton combustion, employing a very low number of deposited layers. To this aim, in the present manuscript, 3BL consisting of an anionic UV-curable polymer doped with APP and cationic chitosan have been initially deposited on cotton by dipping and subsequently cross-linked upon UV exposure, favouring the formation of covalent bonds between the polymer chains (Figure 1). In doing so, an extremely thin coating in which APP is in intimate contact with chitosan within a 3D UV-cured network has been obtained. Such formulation has proven to thermally protect the fabrics in nitrogen and air atmospheres (as assessed by thermogravimetry), promoting cotton self-extinguishing (in horizontal flame spread tests) and a significant increase of its Limiting Oxygen Index (LOI), even after being subjected to washing at 65°C for 1h. In addition, the cross-linked network generated by UV-curing has guaranteed a high chemical stability to the coating that does not hydrolyse or degrades when in contact with a 1M solution of acetic acid or ammonia.

In conclusion, for the first time the present manuscript deals with the two main issues of LbL, proposing an efficient solution based on the joint action of such treatment with UV-curing processes, thus achieving a significant challenge in the scenario of fabric flame retardancy.

2. Experimental Section

2.1 Materials

Cotton with a grammage of 400g/m^2 was purchased from Fratelli Ballesio S.r.l. (Torino, Italy).

Branched poly(ethylene imine) (BPEI, Mw ~25000 by Laser Scattering, Mn ~10000 by Gel Permeation Chromatography, as reported in the material datasheet), chitosan (low molecular weight, presumable < 20000Da, 75-85% deacetylated chitin, as reported in the material datasheet), acetic acid and ammonia (both 1M solution) were purchased from Sigma Aldrich (Milwaukee, WI).

APP (PHOS-CHEK® P30) was purchased from ICL Performance Products, Inc.

A commercially-available UV-curable aliphatic acrylic polyurethane latex, Uceacot® 6558 (PUA, solid content: 50wt.-%), was kindly supplied by Cytec Industries (Italy).

All reagents were used as received for preparing stable water solutions by simple solubilisation, using 18.2 MΩ deionized water supplied by a Q20 Millipore system (Italy). More specifically, for what concerns chitosan, this latter was solubilised in water, adjusting pH to 4 with acetic acid, and kept under magnetic stirring overnight to reach the complete solubilisation. The final concentration was 1wt.-%.

BPEI was solubilised in water at 0.1wt.-% concentration by means of magnetic stirring for 1h; the pH of such solution was kept unchanged (pH=10). In this condition, such polymer contains a lot of positive charges in its chain, thus, is able to guarantee the coating growth better than other types of pre-activation procedures.

As far as PUA is concerned, initially the photo-initiator (Esacure® DP250, kindly supplied by Lamberti, Italy) was added to the Uceacot® 6558 resin in order to have a content of 4wt.-% with respect to the solid resin. Then, APP was added to the mixture containing both resin and photo-initiator in order to reach a content of 1wt.-%. Table 1 lists the concentrations of PUA, photo-initiator and APP employed in the bath for fabric treatment.

Table 1. Concentration of components in UV-curable system

[PUA] [g/L]	[Photo-initiator] [g/L]	[APP] [g/L]
5	0.2	5

2.2 Layer by layer deposition

Prior to LbL deposition, cotton was washed in Marsille soap, ethanol and diethyl ether and subsequently dried. Then, the so-treated fabrics (or Si wafer) were dipped in a BPEI solution (5min) and alternately immersed into the negatively (PUA+APP) and the positively (chitosan) charged solutions; after each adsorption step, the excess solution was removed by the vigorous squeezing of a padder and the fabrics dried in an oven (80°C). The immersion period for the first couple of layers was set at 5min; the subsequent two layers were obtained after 1min dipping (*see* Figure 1). The process was repeated until a total of 3BL were deposited.

At the end of the LbL deposition, such samples were subjected to the photo-chemical curing, using a Hg UV-lamp (F300S from Heraeus Noblelight Fusion UV Inc., USA) in dynamic configuration: to this aim, to this aim, five exposures of 5 s to UV radiation were employed; the radiation intensity on the surface of the sample was 840mW/cm^2, as measured by a UV-radiometer (Power Puck, from EIT Inc., USA). The above conditions have been already optimised in a previous work [27]; in doing so, the complete polymerization of PUA was achieved.

At the end of these treatments, the weight gain on fabrics was around 5%.

In addition, some of these specimens were washed in distilled water at 65°C for 1h under magnetic stirring and once again the weight gain on fabrics was around 5%. No clear sign of coating removal or degradation was observed at the end of washing cycle.

Thus, the samples under investigation are: untreated cotton (coded as COT), cotton treated with 3 bi-layers (3BL sample) and initially treated with 3 bi-layers and subsequently washed in distilled water at 65°C for 1h (3BL_W sample).

2.3 Characterization

The growth of the LbL assembly was monitored using a Frontier FT-IR/FIR spectrophotometer (16 scans and 4cm^{-1} resolution, Perkin Elmer). IR spectra are acquired after each deposition step.

Attenuated Total Reflectance (ATR) Fourier transformed infrared spectroscopy spectra were collected at room temperature in the range 4000-700cm^{-1} (32 scans and 4cm^{-1} resolution) using a Frontier FT-IR/FIR spectroscopy (Perkin Elmer, Italy) equipped with a diamond crystal (depth of penetration 1.66μm, as stated by the Producer).

The surface morphology of untreated and LbL-treated fabrics was studied using a LEO-1450VP Scanning Electron Microscope (imaging beam voltage: 5kV). Untreated and LbL-treated cotton fabrics were cut ($10x10mm^2$), pinned up conductive adhesive tapes and gold-metallized prior to SEM imaging.

Thermogravimetric analyses (TGA) were performed on a TAQ500 thermogravimetric balance from 50 to 800°C (heating rate of 10°C/min) in both nitrogen and air (60mL/min). 10mg samples were placed in open alumina pans, the experimental error was ±0.5% on weight and ±1°C on temperature. These tests were duplicated. The collected data were $T_{onset\ 10\%}$ (temperature at 10% of weight loss), T_{max} (temperature at maximum weight loss), residue at T_{max} and 700°C.

The flammability of the prepared samples has been evaluated in horizontal configuration; the sample ($100x50mm^2$) was ignited from its short side by a 20mm methane flame (flame application time: 5s). The test was repeated at least 3 times for each formulation in order to ensure reproducibility; during the test, parameters such as afterflame time (length of time for which flame persists after the ignition source has been removed on the basis of ISO 13943 [28], expressed in s), afterglow time (length of time for which there is persistence of glowing combustion after both removal of the ignition source and cessation of any flaming combustion, expressed in s), burning rate (mm/s), char length (mm) and final residue (%) were registered.

LOI tests were performed with a FIRE oxygen index apparatus according to the ASTM D 2863 - 06 (2006) standard [29]. The experimental error was 0.5%.

Cone calorimetry (Fire Testing Technology) was employed to investigate the combustion behaviour of square samples ($100x100mm^2$) under $35kW/m^2$ in horizontal configuration, following the procedure described elsewhere [30]. The following parameters were registered: Time To Ignition (TTI, s), peak of Heat Release Rate (PHRR, kW/m^2), Total Heat Release (THR, assessed at the end of the test, MJ/m^2), Effective Heat of Combustion (EHC, MJ/kg), carbon dioxide and carbon monoxide yields ([CO] and [CO_2], kg/kg for both) and their ratio and final residue (%). The test was repeated 4 times for each formulation in order to ensure reproducibility; the experimental error was assessed as standard deviation (σ).

3. Results and discussion

3.1 Coating growth

Coating growth has been followed by FT-IR spectroscopy on Si wafers. Figure 2 reports the intensity surface plot (a) and the intensity of the peak at 1080cm^{-1} as a function of each deposited layer (b) and the 3D projection of a restricted (1800-800cm^{-1}) IR region (c).

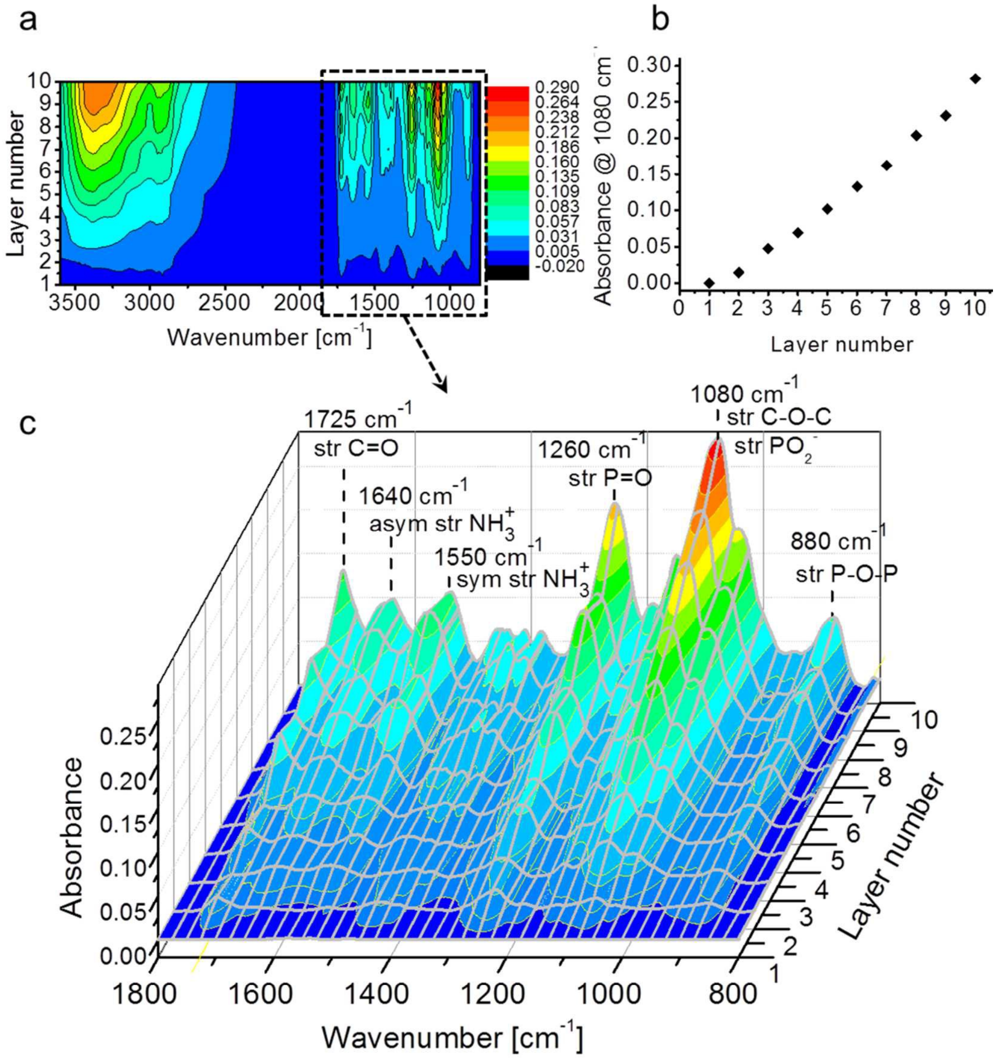

Figure 2. Coating growth followed by IR spectroscopy: a) intensity surface plot at each deposited layer (odd and even numbers corresponding to chitosan and PUA-APP adsorption steps, respectively), b) 1080 cm^{-1} signal intensity as a function of layer number and c) 3D projection of a restricted IR region.

As reported in Figure 2, during the LbL assembly, the characteristic signals of the used reagents proportionally grow after each adsorption step. The presence of chitosan, and thus the coating growth, has been confirmed by the increase of the signal intensity due to the asymmetric and symmetric stretching vibrations of NH_3^+ groups and stretching vibration of glycosidic linkage C-O-C found at 1640, 1550, and 1080cm^{-1}, respectively [31] (Figure 2c). On the other hand, as far as the negative counterparts are concerned, APP signals related to stretching vibrations of P=O, PO_2^- and P-O-P groups have been detected at 1260, 1080 and 880cm^{-1}, respectively. Furthermore, the presence of PUA has been revealed by the peak at 1725cm^{-1} ascribed to the C=O stretching vibration [32]. Finally, the most intense peak at 1080cm^{-1} can be ascribed to both chitosan and APP functional groups; plotting the intensity of such signal as a function of the layer number deposited on Si wafer, a linear growth regime for this assembly has been found, as clearly demonstrated in Figure 2b.

3.2 Chemical and morphological characterization of coatings on cotton

The chemical characterization of the coatings deposited on cotton has been performed by ATR spectroscopy. Figure 3 reports the collected spectra of untreated COT, 3BL and 3BL_W samples.

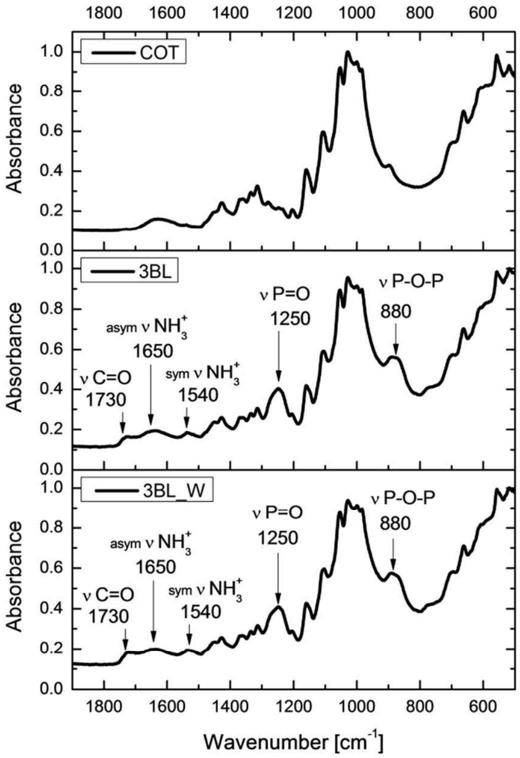

Figure 3. ATR spectra of COT, 3BL and 3BL_W in 1900-500cm^{-1} range.

The main infrared vibrations of chitosan (the positive counterpart in LbL assembly) and substrate are perfectly overlapping due to the similarity of their chemical structure, the only hint that reveals chitosan presence on fabric surface is represented by the appearance of two weak peaks in the 1800-1500cm^{-1} region that are ascribed to asymmetric and symmetric stretching vibrations (1640 and 1550cm^{-1}, respectively) of NH_3^+ groups present in chitosan (Figure 3), as mentioned above (Figure 2c). On the other hand, a more evidenced proof of the occurred deposition of the architectures under investigation can be found in PUA or APP signals. Indeed, the weak peak at 1730cm^{-1} related to C=O stretching vibrations can be attributed to PUA, but better evidence of the occurred deposition can be found in two strong and specific signals at 1245 and 875cm^{-1} for both 3BL and 3BL_W samples; these peaks can be ascribed to stretching of P=O and P-O-P groups present in APP chemical structure.

Further confirmation of the coating deposition can be observed in SEM micrographs reported in Figure 4.

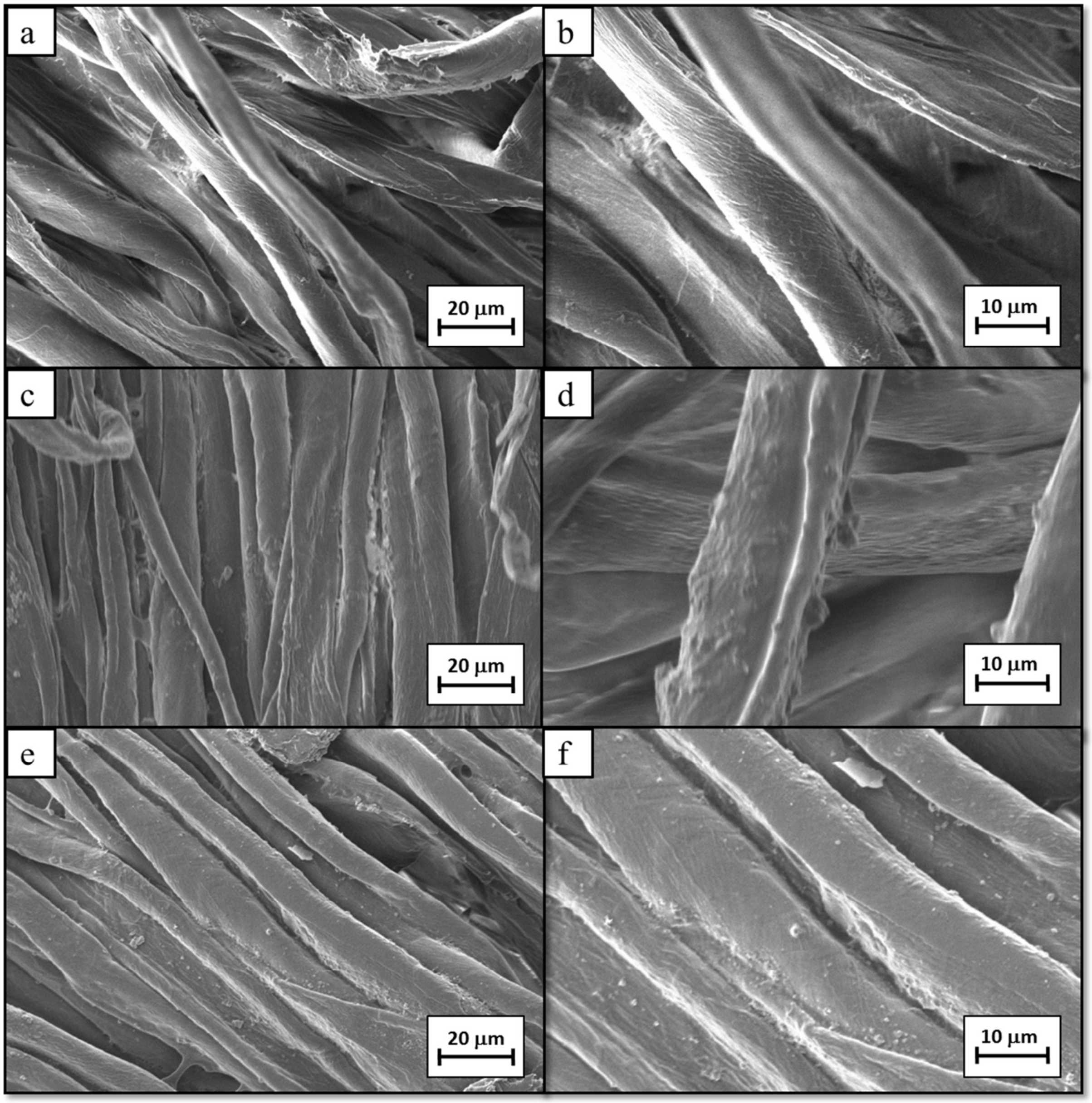

Figure 4. SEM micrographs of COT (a and b), 3BL (c and d) and 3BL_W (e and f).

The typical irregularity and roughness of untreated cotton fibres (well visible in Figures 4a and 4b) disappear when 3BL are deposited on their surface. Indeed, a homogeneous and continuous coating able to regularly and uniformly cover the singular fibres and interconnect the adjacent ones, as well visible in Figures 4c and 4d. When such sample is washed in water at 65°C for 1h, the coating morphology does not change (Figures 4e and 4f); indeed, cotton fibres still appear well covered and interconnected. The cross-linked structure generated by UV-curing processes had guaranteed the coating durability to washing. No phenomena of partial hydrolysis or coating removal/pull out has been detected, according to the fact that after such treatment the weight gain has been kept.

In order to further investigate the coating chemical stability, other two tests of durability in acetic acid and ammonia (1M) at room temperature for 1h have been performed. Once again, after this washing test the coating morphology has been observed by SEM (Figure 5).

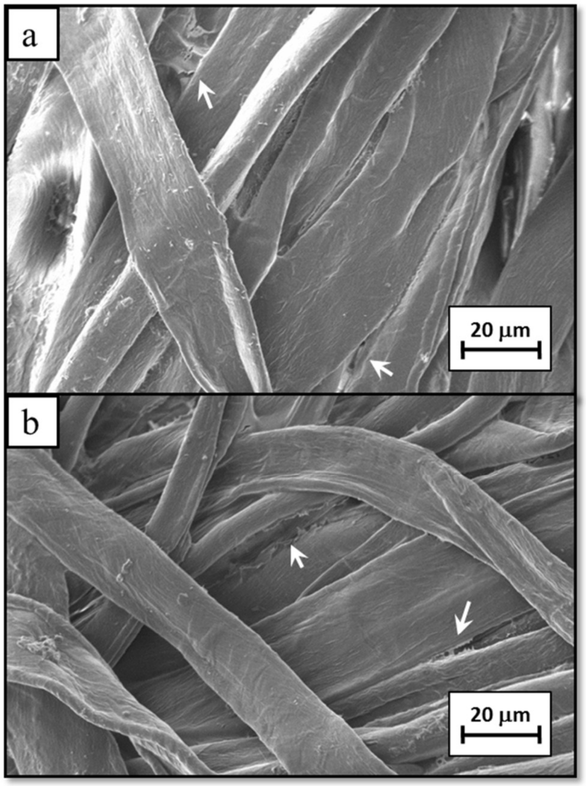

Figure 5. SEM micrographs of 3BL treated with acetic acid (a) and ammonia (b).

The coating under investigation has proven to resist to acetic acid (Figure 5a) as well as to ammonia (Figure 5b), without losing its characteristic morphology. Analogously to what observed for the sample simply washed in hot water, after the treatment with such acid or base, the coatings still cover the singular cotton fibres, maintaining the bridges keeping them contiguous, as pointed out by white arrows in Figure 5.

3.3 Thermal characterization of LbL-treated fabrics

The thermal and thermo-oxidative stability of untreated and LbL-treated cotton fabrics have been investigated by using TGA. Figures 6 and 7 report the TG and dTG curves and Tables 2 and 3 list the collected data in nitrogen and air, respectively.

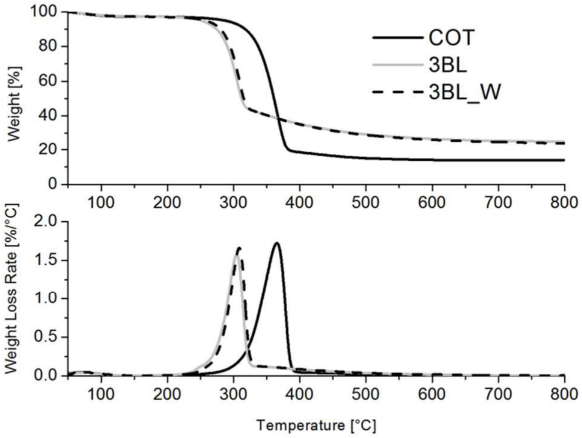

Figure 6. TG and dTG curves of COT, 3BL and 3BL_W in nitrogen.

Table 2. TGA data of untreated and LbL-treated cotton fabrics in nitrogen.

Sample	$T_{onset\ 10\%}$ [°C]	T^{*}_{max} [°C]	Residue at T_{max} [%] (*weight loss %)*	Residue at 700°C [%]
COT	310	365	41.0 *(59.0)*	13.7
3BL	269	305	60.5 *(39.5)*	25.0
3BL_W	276	308	60.4 *(39.6)*	24.5

*From derivative curves.

Upon heating, in nitrogen, cellulose contained in cotton fibres competitively degrades through depolymerization and dehydration pathways [33-36], according to the heating rate adopted during TGA experiments [37]. Generally, it is not possible to distinguish a significant difference between these two decomposition reactions in TG curves as they occur at the same maximum degradation temperature, as in our case (365°C in Table 2). The corresponding weight loss is remarkably high (59.0%, *see* Table 2) and generates a final residue of 13.7% at 700°C.

The coating presence significantly changes cotton degradation profile (Figure 6); indeed, a remarkable sensitisation of cotton degradation [38] has been found for both 3BL and 3BL_W samples, as well visible in $T_{onset\ 10\%}$ reductions reported in Table 2 (269 and 276 vs. 310°C for 3BL, 3BL_W and COT, respectively). This trend is ascribed to APP action that starts to generate phosphoric acid in between 220-270°C [39], favouring dehydration of both cellulose contained within cotton fibres and chitosan with formation of a thermally stable char [21, 25]. By this way, cellulose depolymerization toward the release of fuel and combustible gas species (mainly, levoglucosan, furan and furan derivatives) is inhibited.

Thus, the key factor emerging from the aforementioned results is the char formation due to the deposited coating on cotton fibres. This process has been object of extensive studies in the latter fifty years as it is believed that only favouring the formation of high thermally stable char, cotton flammability can be suppressed [33, 40-47]. The char formed by both 3BL and 3BL_W decomposes at lower maximum temperatures with respect to that left by untreated cotton (305 and 308 vs. 365°C for 3BL, 3BL_W and COT, respectively) but it results more thermally stable, as demonstrated comparing the residues found at T_{max} and at 700°C reported in Table 2. A slight difference has been found between 3BL and 3BL_W residues that however can be considered negligible, taken in account the experimental error of the thermogravimetric balance adopted in the present study.

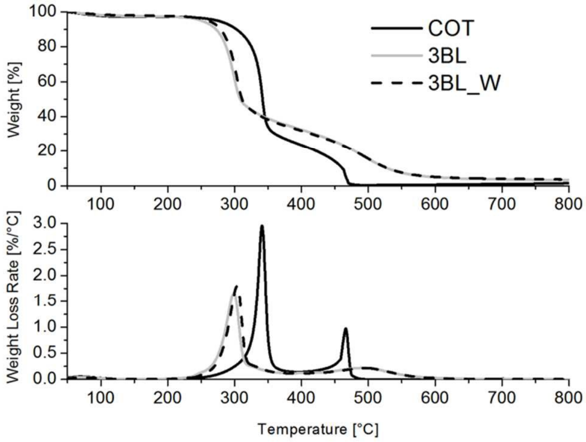

Figure 7. TG and dTG curves of COT, 3BL and 3BL_W in air.

Table 3. TGA data of untreated and LbL-treated cotton fabrics in air.

Sample	$T_{onset\ 10\%}$ [°C]	T^{*}_{max1} [°C]	Residue at T_{max1} [%] (*weight loss %)*	T^{*}_{max2} [°C]	Residue at 700 °C [%]
COT	294	341	53.0 *(47.0)*	466	-
3BL	266	299	61.8 *(38.2)*	494	3.8
3BL_W	274	304	61.1 *(38.9)*	497	4.0

*From derivative curves.

In air, the decomposition mechanism of cellulose does not significantly change as depolymerization and dehydration occur in a single step with a maximum weight loss (47.0%, *see* Table 3), but at lower temperatures (at 341°C) with respect to what happens in nitrogen (Figure 7); in oxidative atmosphere, the char formed after this decomposition is further oxidised at high temperatures (466°C) toward carbon monoxide and dioxide, as widely discussed in the literature [48-51]. Once again, the coating presence strongly sensitised cellulose decomposition (significant differences in $T_{onset\ 10\%}$ values), but at the same time favours the char formation, while greatly slowing down the second with loss step as observable by the significant reduction and shift towards higher temperature of the relative peak in dTG curves (*see* T_{max2} values in Table 3). The final residue at 700°C is increased to about 4% for both 3BL and 3BL_W (Table 3).

3.4 Combustion characterization of LbL-treated fabrics

Focus of the present paper was to deposit few durable layers exploiting the joint action of LbL and UV-curing processes. In order to assess the flame retardant features of the coatings under investigation, three different combustion tests have been performed. More specifically, the resistance to a flame application as well as to a heat flux have been investigated.

In the former case, COT, 3BL and 3BL_W were ignited for 5s by a 20mm methane flame; the collected data are reported in Table 4. This condition simulates one of the most common sources of ignition for fabrics that eventually can lead to fire development.

Table 4. Horizontal flame spread and LOI data of untreated and LbL-treated cotton fabrics.

Sample	Afterflame time ±σ [s]	Afterglow time ±σ [s]	Burning rate ±σ [mm/s]	Char length ±σ [mm]	Residue ±σ [%]	LOI [%]
COT	167±2	35±6	0.80±0.02	100±0.5	-	21.5
3BL	34±14	-	0.65±0.10	22±8	91±3	25.0
3BL_W	72±9	-	0.63±0.02	46±7	85±2	24.0

When untreated cotton is ignited, it starts to vigorously burn (burning rate of 0.80mm/s) and then undergoes afterglow phenomenon after an average afterflame time of 167s, without leaving any final residue. The afterglow phenomenon is represented by the flameless combustion, usually characterized by red glowing, that further consumes what remains of the sample. 3BL and 3BL_W burn more slowly (0.65 and 0.63mm/s) with respect to untreated cotton and reach the self-extinguishing in a short time (34 and 72s, respectively), consuming a limited specimen area (22 and 46mm out of 100mm) and leaving a consistent and coherent final residue (91 and 85%). Indeed, after ignition, the advancing flame gradually reduces in size while being forced, by the presence of the coating, to a progressively smaller portion of the fabric till combustion cannot be sustained anymore and the flame extinguishes. Subsequent flame applications are not able to ignite the sample again. In detail, the heat provided by the flame triggers release of phosphoric acid by APP, which promotes chitosan and cellulose char formation. This is followed by the build-up of a charred coating (made of chitosan) that, combined with the increased char production from cellulose, cut off the release of combustible volatiles feeding the flame.

The significant difference in terms of afterflame time and char length found for 3BL and 3BL_W may be ascribed to some traces of water in 3BL_W. Indeed, if water is absorbed by PUA, the partial swelling of resin may occur; by this way, such sample can burn more slowly for the water presence, increasing the afterflame time, but, at the same time, reducing sample temperature, thus favouring cellulose dehydration toward the char formation [52].

This behaviour is of extreme importance as it means the suppression of a potential fire spread threat; in addition, this self-extinguishing feature is maintained before and after washing, further confirming the durability of the performances imparted by the coating. Figure 8 depicts the final residues of 3BL and 3BL_W samples at the end of these horizontal flame spread tests and some SEM micrographs of the burnt areas. As well visible, the original texture of the fabrics has been maintained and cotton fibres appear only partially damaged by the presence of the flame.

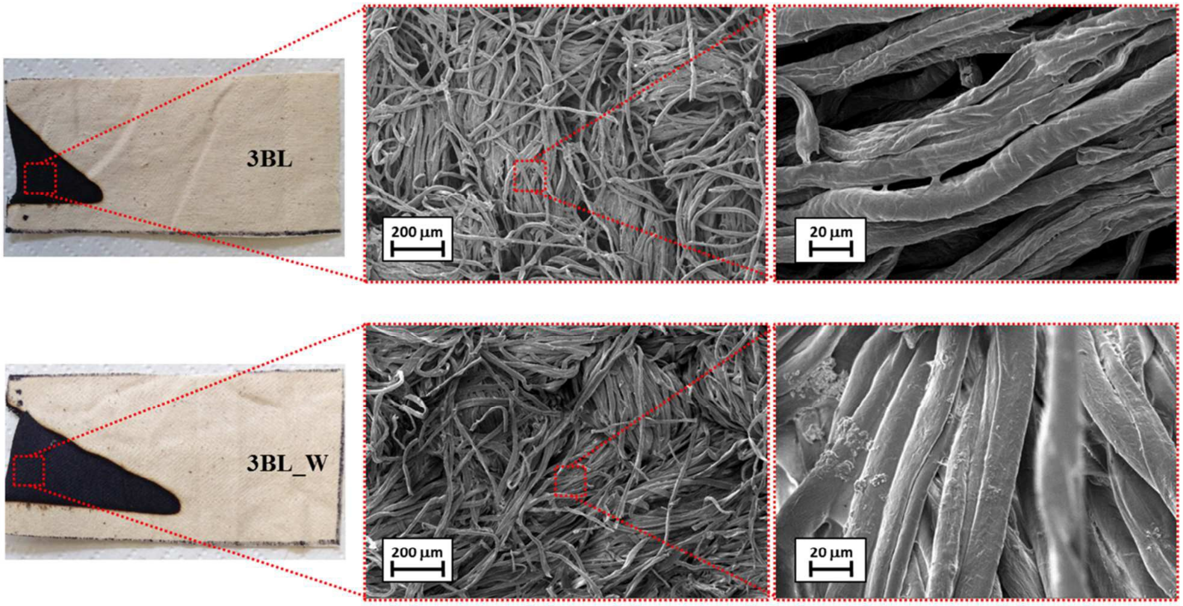

Figure 8. Pictures and SEM micrographs of 3BL and 3BL_W residues after horizontal flame spread tests.

LOI tests have been performed in order to further confirm the good performances described before. Although LOI tests are under debate over and over again for their real significance, they can suggest how a material behaves when ignited as in a "candle-like" test [53]. The results of these tests are reported in the last column of Table 4; as it is clear, the LbL treatment has proven to be efficient for increasing cotton LOI (25.0 and 24.0 vs. 21.5% for 3BL, 3BL_W and COT, respectively); indeed, both 3BL and 3BL_W exhibited a higher LOI value as compared to untreated cotton, although a slight performance lack has been registered when the coating was washed in water.

In order to deeply investigate the context of a real fire scenario, the resistance of COT, 3BL and 3BL_W to a 35kW/m^2 heat flux has been assessed by using cone calorimetry. This test simulates the behaviour of the fabrics when exposed to the heat flux normally found in developing fires. Collected results are reported in Table 5.

Table 5. Cone calorimeter data of untreated and LbL-treated cotton fabrics.

Sample	TTI±σ [s]	PHRR±σ [kW/m^2] *(reduction, %)*	THR*±σ [MJ/m^2] *(reduction, %)*	EHC± σ [MJ/kg] *(reduction, %)*	[CO_2]/[CO]	Residue±σ [%]
COT	27±3	168±5	4.7±0.2	14.8±0.6	56.2	<1.0
3BL	24±2	146±9 *(11)*	3.2±0.3 *(32)*	9.5±0.6 *(36)*	4.5	9.0
3BL_W	22±4	154±10 *(8)*	3.4±0.3 *(28)*	9.5±0.4 *(36)*	4.5	8.0

* Accumulation time at the end of the test was 155s

As evidenced in Table 5, cotton TTI is not significantly affected by the coating presence, regardless of the sample type; indeed, it remains almost constant, taken in consideration the standard deviation. In addition, the combustion rate has been only slightly decreased (-11 and -8% of PHRR for 3BL and 3BL_W, respectively). Conversely, a remarkable reduction of THR (-32 and -28% for 3BL and 3BL_W, respectively) and EHC (-36% for both samples) has been obtained. This trend is due to the coating action that favours the formation of a thermally stable char (according to TGA data), inhibiting the formation of combustible species that may further fuel cotton combustion. By this way, a lower amount of carbon species can burn hence the total heat release and the effective heat combustion of LbL-treated fabrics are lower than those of untreated ones.

This fact can be further proven by monitoring [CO_2]/[CO] ratio: indeed, the reduction of this ratio after the LbL treatment, clearly indicates that the combustion is inhibited/inefficient and the char formation is favoured. According to this assumption, from the data reported in Table 5, we can conclude that the LbL-treated samples tend to form char more than untreated cotton.

From an overall point of view, it is noteworthy that the performances of 3BL_W are comparable with those of 3BL, demonstrating that the UV-curing processes can be a useful treatment for ensuring durability to LbL assembly. Indeed, combining these two technologies, cotton combustion suppression has been achieved with only few durable layers.

4. Conclusions

The present manuscript demonstrates that it is possible to suppress cotton combustion with only few durable layers by combining Layer by Layer assembly with UV-curing processes.

The performances of 3 bi-layers consisting of the alternation of a UV-curable aliphatic acrylic polyurethane latex doped with ammonium polyphosphate (negative counterpart) and chitosan (positive counterpart) have been compared with those of the same assembly subjected to washing cycle at 65°C for 1h. The results showed that both coatings are very efficient to protect cotton from i) the heat and oxygen (from thermogravimetry), ii) a 20mm methane flame (from horizontal flame spread tests), iii) a 20mm propane flame (from LOI tests) and iv) a heat flux of 35kW/m^2 (from cone calorimetry). Indeed, thanks to their char-former character, both these coatings allowed suppressing cotton combustion in horizontal configuration, increasing its LOI and reducing the total heat release and effective heat of combustion when exposed to 35kW/m^2. The assemblies described here provide a green and sustainable way for the production of durable fire protective coatings characterized by high efficiency at low number of deposition steps that could be possibly exploited and extended to other substrates.

Acknowledgment

The Authors want to thank Mr. Fabio Cuttica (for cone calorimetry tests) and Mrs. Giuseppina Iacono (for SEM analyses). In addition, the Authors thank the European COST Action FLARETEX (MP1105) “Sustainable flame retardancy for textiles and related materials based on nanoparticles substituting conventional chemicals”.

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