Starch-Based Layer by Layer Assembly: Efficient and Sustainable Approach to Cotton Fire Protection

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S *Supporting Information*

ABSTRACT: Starch has been employed via layer by layer assembly for building an efficient and sustainable biobased coatings capable of protecting cotton from fire. In order to obtain a better understanding of the coating to substrate relationship, the coating efficiency has been tested on cotton fabrics having different densities (i.e., 100, 200, and 400 g/m^2). The adopted deposition conditions allow for the buildup of a homogeneous coating even at a low number of deposition steps. The physical and chemical mechanisms are described and related to the achieved results. The coating can greatly enhance the char forming ability of cellulose, nearly doubling the amount of thermally stable organic residue produced by cotton at high temperatures, as assessed by thermogravimetric analyses. After only 2 bilayers deposited, this biobased system is capable of self-extinguishing a flame during flammability tests with less than 5% in weight deposited on cotton. This high efficiency is kept even when the coating is deposited on cotton with the highest density. By cone calorimetry, all treated cottons showed significant reductions (up to 40%) of the total heat released during combustion, thus demonstrating the high efficiency achieved.

KEYWORDS: layer by layer, biobased materials, starch, thermal stability, fire protection
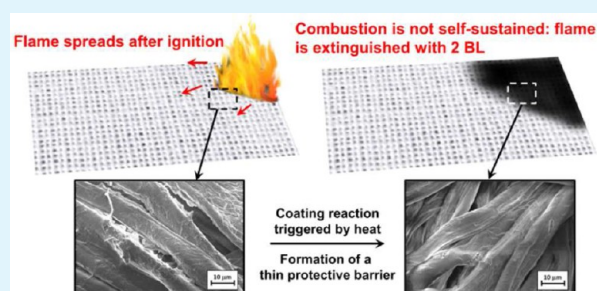
INTRODUCTION

Nowadays, the fire protection field is facing critical time as the safety and efficiency of the chemistry normally adopted in such field have been questioned. Indeed, over the past decade, an increasing number of studies and publications reported about the long-term toxicity hazard of some widely used halogenated species.[1] These have been found out to be persistent in the environment, dangerously ending up in the food chain and eventually discovered in the bodies of animals and humans. Countermeasures to this situation lead to the limitation in use or complete removal of the chemicals for which hazard has been proven and the start of a campaign aiming to scrutiny the benefit over danger ratio for the remaining flame retardants.[2] In such a worldwide scenario, nontoxic and, possibly, green solutions are thus of both interest and need.

Among the possible solutions the layer by layer (LbL) deposition technique made the concept of surface nano-structuring for fire protection possible.[3] Indeed, the surface plays a key role in ignition and combustion of polymers because, being the interface between gas and condensed phase, it controls mass and heat transfers. The heat reaching the polymer surface is transmitted to the bulk, from which volatile products of thermal degradation diffuse toward the surface and the gas phase, feeding the flame. By controlling this interface, it is thus possible to control the burning behavior of a polymer. In

this scenario, the ability of finely structure the surface granted by the LbL technique proved to be interesting and extremely efficient.[4] Indeed, the so-called LbL, can be considered as a very simple but powerful tool that allows the build up of nanostructured coatings on the basis of one or more interactions taking place between the selected reagents.[5] The most common and widely used interaction is the electrostatic attraction that takes place between oppositely charged polyelectrolytes or nanoparticles;[6] several other interactions, such as donor/acceptor,[7] hydrogen bonds[8] and covalent bonds,[9] are also possible. The reagents are deposited from a solution dipping (or spraying) process which outcome can be easily tuned up by controlling parameters such as chemicals chemistry,[10] solution pH,[11] temperature,[12] and ionic strength.[13]

In the last five years, the LbL has been successfully adopted for the buildup of thermally insulating and fire shielding coatings made of inorganic nanoparticles or hybrid organic–inorganic systems.[14−17] Since the first preliminary studies, great progress has been made; the coating efficiency has been increased allowing better and sometimes unmatched properties. Indeed, considering cotton as an example, the achieved
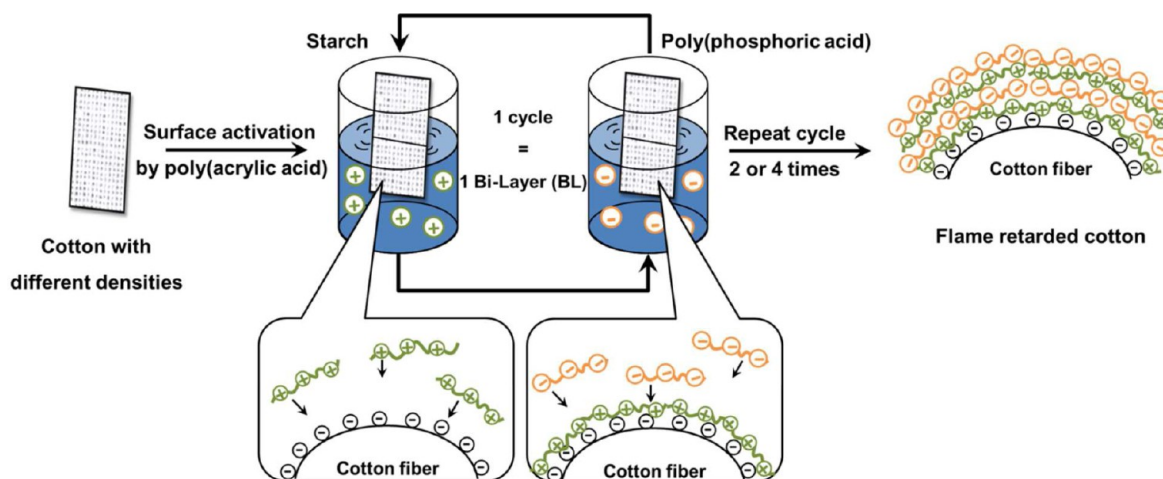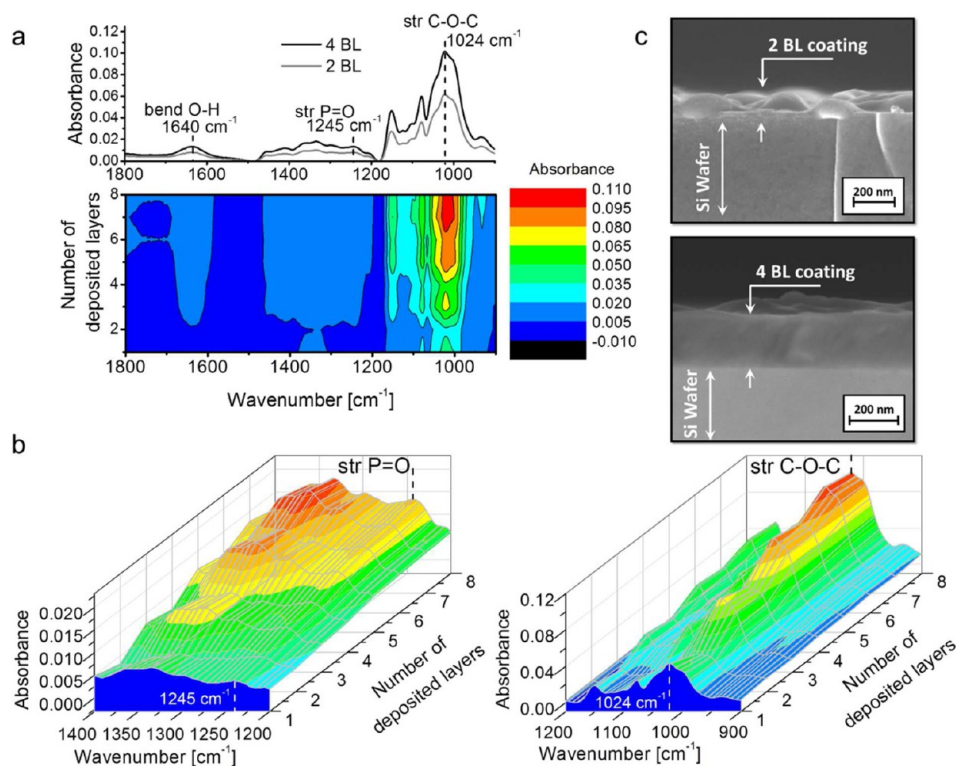
Figure 1. Schematic representation of the adopted LbL assembly. Cotton fabrics are preactivated by poly(acrylic acid) and then alternatively dipped in the starch (positive) and poly(phosphoric acid)(negative) solutions. The process is repeated 2 or 4 times in order to deposit 2 or 4 Bi-Layers (BL), respectively.

Figure 2. Coating growth followed by IR spectroscopy: (a) IR spectra at 2 and 4 BL and intensity surface plot at each deposited layer (odd and even numbers corresponding to starch and PPA adsorption steps, respectively), (b) 3D projection of restricted IR region, and (c) Si wafer cross section of the coating at 2 and 4 BL.

performances evolved from systems that could barely preserve the structure of the fabric after flammability tests to structures capable of self-extinguishing a flame, maintaining most portion of the fabric intact.[18,19] The number of reagents and substrates has been increased embracing different kinds of nanoparticles or green polyelectrolytes that have been deposited on fabrics, foams, and thin films.[20−26] The parameters controlling the deposition have been studied allowing a better understanding of the coating morphology/final properties relationship.[21,27,28]

However, one of the parameters that is currently limiting LbL application is the high number of deposition step often needed in order to reach the desired properties. As an example,

coatings deposited by LbL for protecting cotton often need 20−40 deposition steps in order to achieve significant flame retardant properties (e.g., self-extinguishment during flammability tests or significant reduction of the heat release rate during combustion).[29]

In the present paper, we are presenting high efficiency LbL coatings based on starch capable of conferring self-extinguishing behavior to cotton after only 4 or 8 deposition steps. To this aim, cationic starch has been coupled with poly(phosphoric acid) (PPA) and assembled on fabrics following the scheme reported in Figure 1.
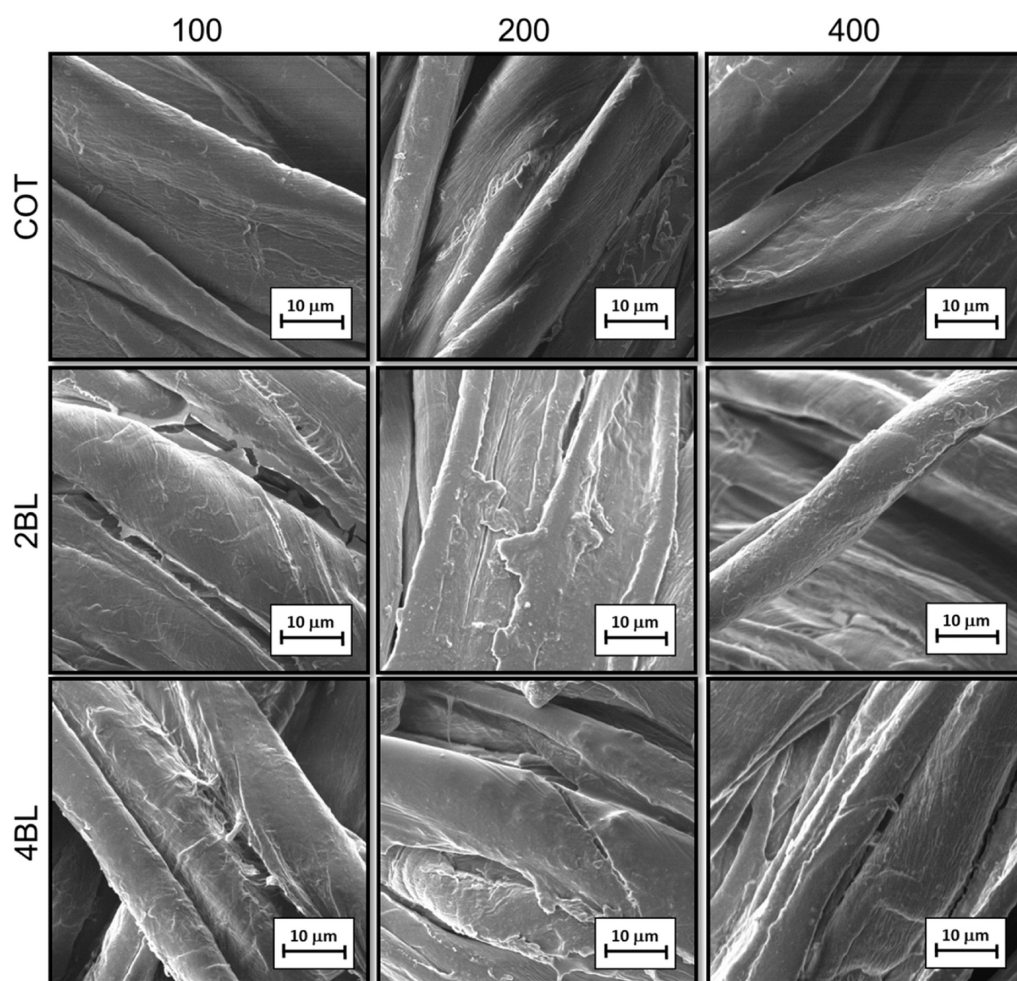
Figure 3. SEM micrographs of untreated and LbL-treated COT 100, 200, and 400.

In the proposed system, starch and PPA can react to together when exposed to a flame or a heat flux in order to create a protective coating on the fiber surface. The starch is able to produce a thermally stable carbonaceous structure (*char*) upon heating;[30−33] this ability is further enhanced by the dehydration abilities of the polyphosphoric acid.[34] While PPA has already been employed in LbL coatings for fire protection, starch has never been selected as a coating constituent; moreover, the proposed LbL architecture represent a sustainable and environmentally friendly solution in compliance with current societal demands. In addition, the efficiency of the coating has been thoroughly evaluated on cotton fabrics bearing different densities (i.e., 100, 200, and 400 g/m^2). Although never studied, this aspect can be of fundamental importance; indeed, by increasing the density the amount of substrate that needs protection greatly increases, while the surface available for the LbL deposition is almost unchanged. As a consequence, the coating efficiency has to be extremely high in order to protect an increased amount of combustible material.

The coating growth and morphology on cotton have been assessed by infrared spectroscopy (IR) and scanning electron microscopy (SEM), respectively. Then, the thermal and thermo-oxidative stability of treated fabrics has been measured by thermogravimetric analysis (TGA) in inert and oxidative atmospheres. Pyrolysis-combustion flow calorimetry (PCFC) tests have been performed and compared to TGA data in order to provide additional information.

Flame retardant properties have been tested by assessing the reaction to a direct flame application (i.e., flammability tests) and to an irradiative heat flux (i.e., cone calorimetry tests).

The deposition of only 2 BL of this starch/PPA coating imparts self-extinguishing behavior to the treated substrate regardless of the adopted density. After combustion, SEM observation reveals the presence of almost undamaged fabric texture and fibers.

RESULTS AND DISCUSSION

Coating Growth and Morphology on Cotton. The coating growth has been assessed by transmission infrared spectroscopy. Figure 2 reports the acquired IR signals at 2 and 4 BL, the intensity surface plot as a function of each deposited layer, the 3D projection of restricted IR region, and the Si wafer cross section of the coating at 2 and 4 BL.

Pure starch shows characteristic signal around 1640 cm^{-1} ascribed to O—H bending of water and broad bands from 1300 to 1440 cm^{-1} assigned to CH$_2$ groups.[35] Intense bands appear from 900 to 1200 cm^{-1} corresponding to the C—O bond signals, the most intense is due to glycoside linkage C—O—C stretching.[35] Neat poly(phosphoric acid) (PPA) shows characteristic peaks around 1200, 1000, and 885 cm^{-1} attributable to the stretching of P═O, P—O, and P—O$^-$ groups, respectively; a broad band, due to OH deformation vibration, can be detected around 1600 cm^{-1}.[36]

When the two components are LbL assembled on Si wafer, the signals characteristic of both components grows proportionally to the deposited layers as reported in Figure 2a specific spectral regions, concerning P=O signal for PPA and glycoside linkage C—O—C shows in details the change of such signals as a function of layer number. As far as PPA is concerned, the P=O signal found around 1245 cm^{-1} grows systematically after the adsorption of each negative layer (even numbers) and remains unchanged after the adsorption of the positive layer. However, the glycoside linkage signal of starch shows a different behavior. Indeed, although this signal grows at each starch adsorption step (odd numbers) its intensity is slightly diminished after each PPA deposition as clearly depicted in Figure 2b. Such behavior can be explained with either a partial desorption of starch or a rearrangement (shrinkage) of the coating structure. FE-SEM observations performed on the cross section of 2 and 4 BL treated Si wafers, reveals the morphology of the coating. After 2 BL, this system can yield a quite thick coating capable of homogeneously cover the surface with a peculiar morphology characterized by hills and valleys resembling an island growth regime. Such morphology is lost after the deposition of 4 BL that yield a thicker and smother coating. Even at such low BL numbers, the coating appears to be quite thick, this can be ascribed to the adopted deposition conditions (i.e., temperature is kept at 60 °C) during the adsorption step of starch.

The coating can be easily deposited on the surface of cotton, as can be observed in Figure 3 that reports SEM observation of untreated and LbL treated cotton fabrics.

The untreated cotton presents a morphology typical of natural fibers with rough surfaces and fibers of irregular shape, as reported in Figure 3. This is consistent for untreated COT100, 200, and 400. The LbL deposition is capable of changing such morphology, regardless of cotton density that does not appear to influence the coating growth. Indeed, after the deposition of 2 BL, the fibers appear coated by a thin and homogeneous coating that sometimes can be also found joining adjacent fibers. The further increase in BL number results in an increased coating thickness while keeping a good surface coverage. Although the formation of a coating bridging adjacent fibers is observed, at such low BL number (i.e., 2 and 4), this does not change the fabric softness. Indeed, as observable in Figure 3, these very thin connections are often broken and not present in all the fibers. The weight gain on fabrics was around 5 and 7% for 2 and 4 BL, respectively.

Thermal and Thermo-Oxidative Stability. The thermal and thermo-oxidative stability of untreated and LbL-coated samples was assessed by thermogravimetric analyses in nitrogen and air, respectively. The aim is to obtain more fundamental degradation information, useful for the understanding of the effects and possible interactions of the deposited coatings on cotton thermal and thermo-oxidative degradation.

Since the presence of the coating yielded similar results, regardless of the adopted cotton density, only the plots concerning COT 100 samples are reported in the figures for clarity; TG and dTG plots for untreated and LbL treated COT 200 and 400 can be found in the Supporting Information, SI (Figure S2, S3, S4, and S5).

Figure 4 reports TG and dTG curves of untreated and LbL-treated COT 100-based samples in nitrogen. Table 1 collects TGA data obtained from the plots of all system.

First, thermal degradation is evaluated in nitrogen environment (no oxidation). Also reported in the literature, the
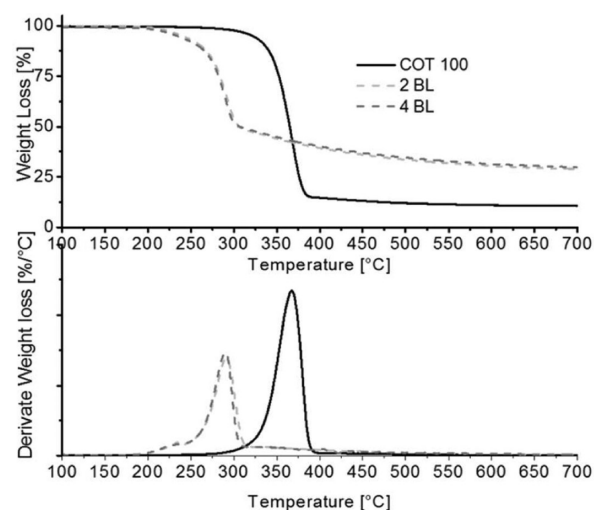
Figure 4. TG and dTG plots of untreated and LbL-treated COT 100-based samples in nitrogen.

**Table 1. Thermogravimetric Data of Untreated and LbL-Treated Samples in Nitrogen**

sample	$T_{onset10\%}$ [°C]	T_{max} [°C]	residue at 700 °C [%]
COT 100	337	367	11
2 BL	259	290	29
4 BL	259	290	30
COT 200	325	365	13
2 BL	258	291	29
4 BL	258	291	30
COT 400	287	337	20
2 BL	261	293	28
4 BL	261	293	28

^{a}From derivative TG curves.

thermal degradation of cellulose proceeds by one step of weight loss, found between 300 and 400 °C that is the result of two competitive processes involving the glycosyl units.[35] The first one is the depolymerization of such units to volatile products (mainly, levoglucosan, furan, and furan derivatives) and it is in competition with the dehydration of the same units to give a thermally stable aromatic char (the final residue collected at the end of the test is 11%).

LbL-treated cotton still presents a one-step thermal degradation; surprisingly, 2 and 4 BL curves almost overlapped showing similar behavior (that is consistent among the different cotton employed). The presence of the LbL coating is responsible for a strong anticipation in the degradation process (see T_{onset} and T_{max} values in Table 1). Such anticipation is ascribed to the PPA, and it is considered a positive phenomenon; indeed, the release of phosphoric acid by PPA favored the cellulose decomposition toward char formation, thus resulting in the production of less volatile and combustible materials.[37−39] The same effect occurs on the starch within the coating and allows for the formation of a thermally insulating char layer that further promotes the cellulose char formation, by limiting heat transfer and hindering volatiles release. As a consequence of this combined effect, the final residue is extremely high (30%). Such finding can be extended to all treated cottons (see Table 1), and it is of extreme importance as it can be achieved after the deposition of only 2 BL.

The thermo-oxidative stability was also evaluated by TG analyses performed in air; furthermore, pyrolysis-combustion flow calorimetry (PCFC) has been compared with TG data in order to better investigate the high char forming efficiency exhibited by the starch/PPA LbL coating. During PCFC tests the cotton is pyrolyzed and the resulting combustible volatile gases are burned in the presence of an air environment, yielding a heat release rate signal (HRR) as a function of temperature thus providing information on the flammability of the volatiles released (the higher the HRR the higher the flammability).[40] This has been proven to be a valuable and complementary comparison for assessing the presence of an effect capable of increasing cotton char forming feature.[41] Figure 5 reports TG, dTG, and HRR plots for COT 100-based systems and Table 2 collects the data calculated from TGA and PCFC.
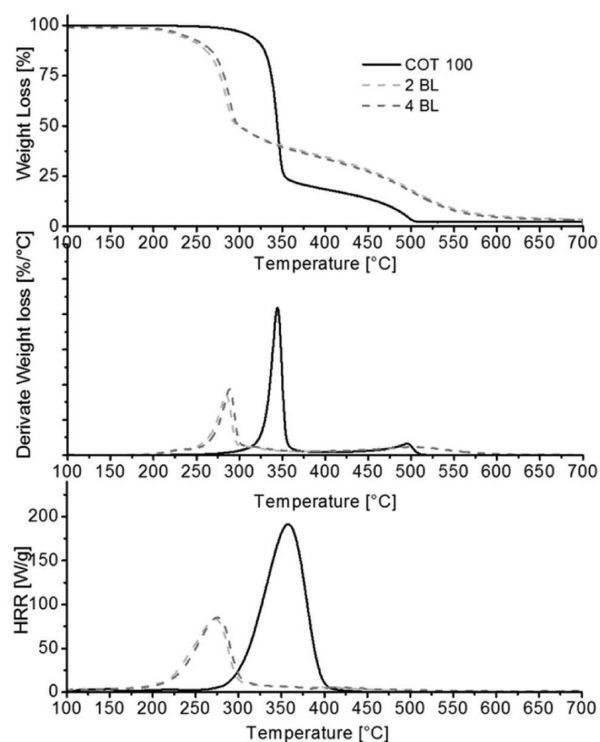
Figure 5. TG, dTG (in air), and HRR plots of untreated and LbL-treated COT 100-based samples.

As can be observed from Figure 5, the thermal oxidation of cotton occurs in two steps. The first, in the range between 300

and 400 °C, is due to the formation of both volatiles and aliphatic char (18%).[42−44] This char is then oxidized to CO and CO_2 during the second step leaving almost no residue. As already observed in nitrogen, LbL treated cotton displayed an anticipation in the degradation due to the presence of PPA. Again, the effects of PPA on cotton char formation and the interaction with starch for the buildup of an insulating coating results in an improved char formation during the first decomposition steps (residue at 400 °C is almost doubled for 2 and 4 BL as reported in Table 2). Such residue is then gradually oxidized at higher temperatures. COT 200 and COT 400 systems displayed similar behavior, as reported in Table 2 and SI (Figure S2). PCFC measurements confirm the improved char forming ability exhibited by LbL-treated samples (Figure 5, HRR plots). Indeed, the HRR curves, and related peak, appear to be strongly reduced for 2 and 4 BL (peak reduced by 55%). COT 200-based samples achieved similar reductions (−50%) while for COT 400 the efficiency of the coating appears to be reduced only yielding about 10% reduction (see Table 2). This can be certainly ascribed to the increased density of the substrate that is thus more difficult to protect. Total heat release shows reduction trends similar to those of heat release rate peak.

Flame Spread Tests. In order to assess the propensity of the untreated and LbL-treated fabrics to initiate a fire, the reaction to a direct methane flame application needs to be assessed. For this reason flame spread tests in horizontal configuration were carried out; Table 3 reports observations during the test, while snapshots of the residues after the test are collected in SI (Figure S6).

Table 3. Flammability Data from Horizontal Flammability Tests of Untreated and LbL-Treated Samples

sample	combustion rate [cm/s]	afterglow	residue [%]
COT 100	0.17	yes	0
2 BL	0.13	no	79
4 BL	0.15	no	71
COT 200	0.13	yes	0
2 BL	0.11	no	74
4 BL	0.13	no	59
COT 400	0.10	yes	11
2 BL	0.05	no	75
4 BL	0.05	no	73

Upon methane flame application, untreated cotton ignites immediately and quickly burns with vigorous flames. Then the

Table 2. Thermogravimetric Data in Air and Pyrolysis-Combustion Flow Calorimetry Data of Untreated and LbL-Treated Samples

| sample	$T_{onset10\%}$ [°C]	T_{max1} [°C]	T_{max2} [°C]	residue at 400 °C [%]	PHRR [W/g] (reduction, %)	THR [kJ/g] (reduction, %)
COT 100	326	345	495	18	190	11.6
2 BL	254	285		35	85 (−55)	5.6 (−52)
4 BL	260	289		34	85 (−55)	5.6 (−52)
COT 200	313	342	464	23	153	11.1
2 BL	254	290		35	81 (−47)	5.9 (−47)
4 BL	258	290		34	74 (−52)	5.9 (−47)
COT 400	280	310	405	20	94	8.1
2 BL	266	298		31	86 (−8)	6.7 (−17)
4 BL	266	294		32	85 (−9)	7.2 (−11)

[a]From derivative TG curves.
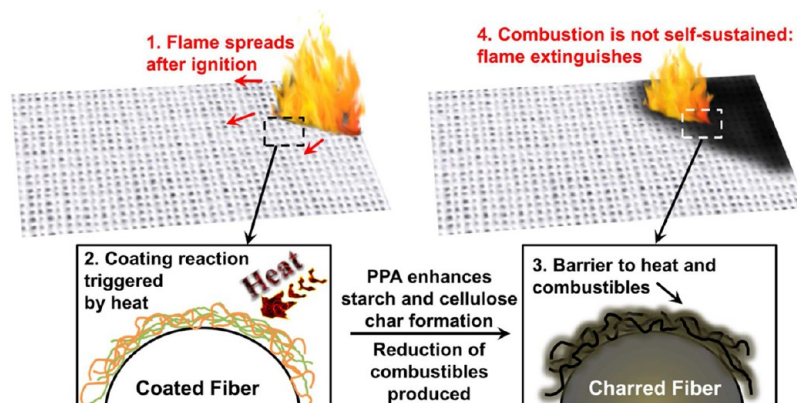
Figure 6. Schematic representation of the starch/PPA coating action during horizontal flame tests.

flame spreads, rapidly reaching the opposite edge of the sample where it vanishes and is replaced by the afterglow phenomenon. This latter is defined as flameless combustion, characterized by red glowing, that further consumes the sample. Although the flame is not present, the high temperatures reached during the afterglow can still spread the fire to other ignitable and flammable materials, thus representing a safety threat. Untreated COT 100 and COT 200 leave no residue after the test, while COT 400 displayed a 11% residue as well as a reduced burning speed with respect to the lighter fabrics.

The presence of the LbL coating dramatically changes cotton burning behavior. Indeed, after the deposition of only 2 BL, a self-extinguishing behavior is obtained. After ignition, the spreading flame is gradually reduced in size, and it is forced to a progressively smaller portion of the fabric where eventually extinguishes. Furthermore, any subsequent flame application cannot ignite the sample again. Figure 6 reports a schematic representation of the coating action during the test.

The heat transmitted by the advancing flame triggers the coating reaction: the phosphoric acid provided by PPA promotes the formation of a protective barrier and, at the same time, enhances the cellulose char formation, as already observed in TGA and PCFC measurements. These two effects combined together reduce the production of combustible volatiles that feed the flame, combustion cannot be self-sustained and a self-extinguishing behavior is observed. Such behavior is of fundamental importance since is consistent among all treated cottons and could represent the suppression of a potential fire threat; as a consequence of this self-extinguishing behavior, the residues left after combustion are extremely high as reported in Table 3. It is important to mention that this extinguishing results have been achieved in the literature after five times the number of deposition steps presented in this paper, namely 10 BL (or 5 QL).[20,45] The deposition of 4 BL does not increase the efficiency of the coating; although the self-extinguishing behavior is still reached, this takes place in longer times, thus preserving a reduced portion of the fabrics (see residues % in Table 3 and snapshots of the residues in SI Figure S6). It seems that the efficiency of the coating reaches a maximum after 2 BL that always yielded the best results, regardless of the adopted substrate.

Analysis of Char Residue. The residues collected after flammability tests were investigated by SEM in order to assess the changes in morphology and composition due to the flame. Figure 7 reports the acquired micrographs taken from undamaged and burned region of 2 BL samples.
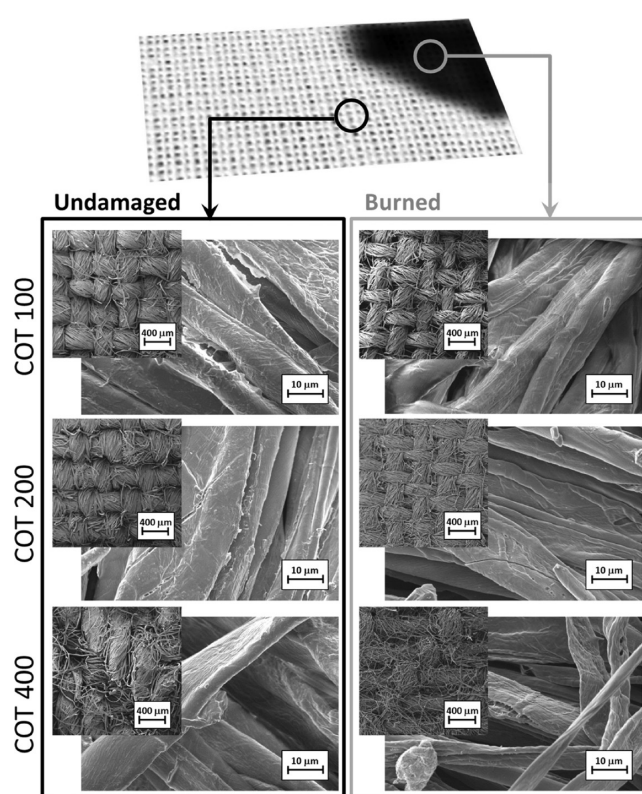

Figure 7. SEM micrographs performed on undamaged and burned regions of 2 BL-treated COT 100, 200, and 400 samples after flammability tests.

As can be clearly detected from Figure 7, the coating barrier action during flammability tests maintained the original fabric texture. The efficiency of the coating was so high that by direct comparison of low magnification micrographs it is almost impossible to discriminate between the undamaged and burned region of the samples. This difference becomes more clear at higher magnifications, where the reduced size of the fibers and the presence of fiber debris clearly points out the after combustion morphology. Notwithstanding this, it is evident that this starch/PPA coating can preserve the fiber structure by improving the char-forming feature of cotton, as described in previous sections. The chemical nature of such residue has been investigated by ATR spectroscopy. The ATR spectra performed on the residues (SI Figure S7) suggest the formation of an aromatic carbonaceous structure (signals at 1580 and 880

Table 4. Cone Calorimetry Observations of Untreated and LbL-Treated Samples

sample	TTI [s]	pkHRR [kW/m²]	THR [MJ/m²]	CO_2/CO [kg/kg]	residue [%]
COT 100	23 ± 2	80 ± 2	1.5 ± 0.1	41	0
2 BL	10 ± 3	56 ± 5	0.9 ± 0.1	5	9
4 BL	12 ± 4	52 ± 12	0.9 ± 0.2	5	9
COT 200	19 ± 2	118 ± 4	2.3 ± 0.3	29	0
2 BL	12 ± 1	96 ± 2	1.6 ± 0.1	5	8
4 BL	16 ± 4	89 ± 8	1.7 ± 0.1	5	8
COT 400	19 ± 4	173 ± 14	4.2 ± 0.2	46	2
2 BL	15 ± 2	150 ± 3	3.1 ± 0.1	5	6
4 BL	16 ±	156 ± 4	3.1 ± 0.1	5	7
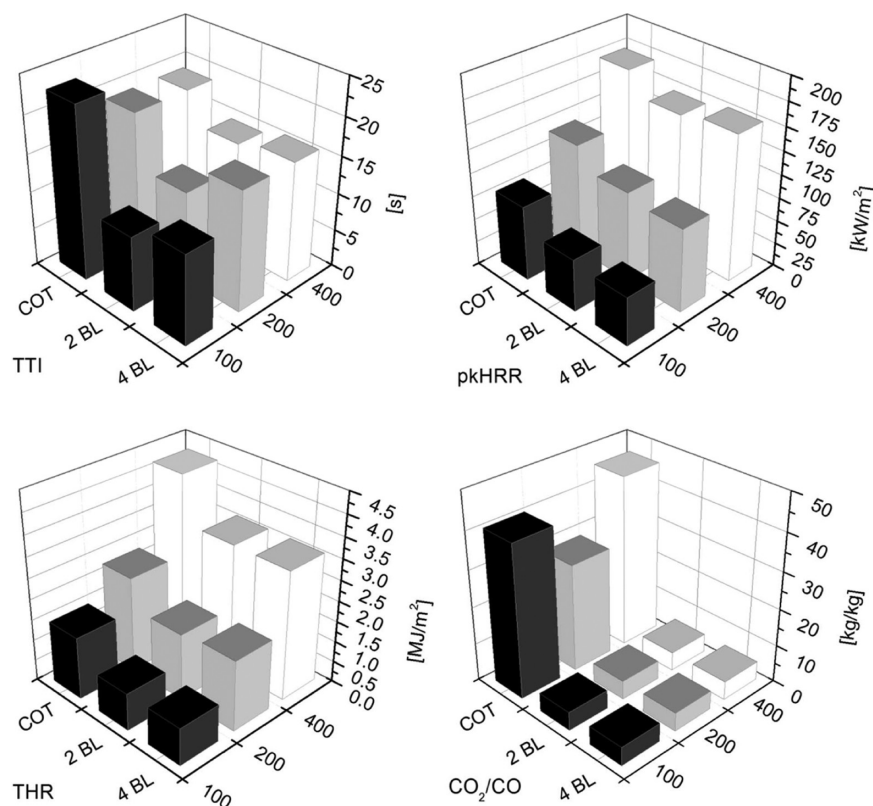
Figure 8. Main cone calorimetry parameters observed for untreated and LbL-treated COT 100, 200, and 400 samples: Time To Ignition (TTI), peak of Heat Release Rate (pkHRR), Total Heat Released (THR), and CO_2/CO ratio (CO_2/CO).

cm^{-1}).[46] Phosphates can be detected as well (signal at 1160 cm^{-1}). However, the presence of carboxyl groups (1700 cm^{-1}) and the absence of triplets in the 900−700 cm^{-1} region (typical of charred structures) suggest the formation of aromatic structures with different substitution degrees.

Cone Calorimetry. Cone calorimetry tests have been performed in an effort to simulate a realistic fire scenario and provide a complete flame retardant characterization. Different from flammability, during cone calorimetry tests, samples are exposed to a heat flux, rather than a small flame, that is normally found in developing fires (35 kW/m²). As a consequence of the high temperature reached, the sample starts degrading and releasing combustible volatile gases. After a certain amount of time, such gases lead to the ignition of the sample and its subsequent flaming combustion. Table 4 lists the main parameters observed during cone calorimetry tests while Figure 8 reports 3D histograms overview of the same parameters.

Figure 8 reveals the presence of the LbL coatings reduces the TTI values, thus anticipating the ignition. This can be linked to the change imparted by LbL coatings to the radiative properties of the material or, as already observed and discussed from TGA data, ascribed to the coating action that anticipates degradation for quickly creating a protective layer on cotton surface. The result of this protective layer is to slow down combustion, as demonstrated by the pkHRR values, eventually reducing the total heat evolved. The best results are achieved, after only 2 BL, on COT 100 with 30 and 39% reductions in pkHRR and THR, respectively. COT 200 still shows substantial improvements in both parameters (see SI Table S1) while COT 400 only displayed reduced THR values (−25%).

The monitored production of CO and CO_2 provides additional information. Indeed, the ratio between CO_2 and CO produced during combustion can be considered as a marker of the combustion efficiency. High ratios indicate an efficient combustion (and the heat released) while low ratios are related to inefficient and hindered combustion. As reported

in Figure 8, the CO_2/CO ratio is considerably lowered for all LbL treated fabrics thus further confirming the efficacy of the coating in hindering combustion favoring the formation of thermally stable organic structures in spite of combustible volatile gases. This increases the amount of residue left after combustion; indeed, while untreated cotton is completely destroyed, all LbL treated fabrics left a coherent residue after the tests (see residue values in SI Table S1).

CONCLUSIONS

The present work presents, for the first time, the use of starch in layer by layer coating for surface protection of cotton. Starch has been coupled with poly(phosphoric acid) in order to obtain a sustainable, biobased and high efficient system. Moreover, the efficiency of the coating has been tested on cotton fibers bearing different densities (i.e., 100, 200, and 400 g/m^2) allowing for a better understanding of the coating to substrate relationship. IR spectroscopy coupled to FE-SEM observations demonstrate that this system can yield homogeneous and starch rich coating at low number of deposited bilayers (i.e., 2 and 4). Then, the properties of the coated fabrics have been evaluated revealing the physical and chemical mechanisms occurring between the coating and the cotton. Thermogravimetric analyses showed a greatly enhanced char forming ability; the presence of the coating nearly doubled the amount of thermally stable organic residue produced at high temperatures. Surprisingly, after only 2 bilayers deposited, this biobased system is capable of self-extinguishing a flame during flammability tests with less than 5% in weight deposited. This high efficiency is kept even when the coating is deposited on the highest density cotton. Cone calorimetry further confirms the extremely interesting efficiency achieved. The coating efficiently hindered combustion and significantly reduced the total heat released during combustion. Finally, the described layer by layer assembly makes it possible for a further step toward high efficient and green fire protection solutions to be exploited and extended to several substrates.

EXPERIMENTAL SECTION

Materials. Cotton with different densities (i.e., 100, 200, and 400 g/m^2, hereafter coded as COT 100, COT 200, and COT 400) was purchased from Fratelli Ballesio S.r.l. (Torino, Italy). Branched poly(ethylene imine) (BPEI, $M_w \approx$ 25 000 by Laser Scattering, $M_n \approx$ 10 000 by Gel Permeation Chromatography, as reported in the material datasheet), poly(acrylic acid) (solution average $M_w \approx$ 100 000, 35 wt % in H_2O) and poly(phosphoric acid) (115%) were purchased from Sigma-Aldrich (Milwaukee, WI). Cationic starch (Amylo N-460, 60% of amylose content) was purchased from Roquette, France.

All reagents were used as received for preparing 1 wt % water solutions, using 18.2 MΩ deionized water supplied by a Q20 Millipore system (Milano, Italy). BPEI was employed at 0.1 wt %. Starch solution was prepared by heating up the suspension to 60 °C in order to have a stable solution; this temperature is kept during the LbL process.

Layer by Layer Deposition. Prior to LbL deposition the substrates have been surface activated. Cotton fabrics were dipped in a 1 wt % PAA solution (5 min). Si wafers were dipped in a 0.1 wt % BPEI solution (5 min) and then in a 1 wt % PAA solution (5 min) in order to mimic the same surface activation step used for cotton substrates. Both surface activation treatments prepare the surface fort the subsequent

starch/PPA LbL deposition. Then, Si wafer or cotton fabrics were alternately immersed into the positively (starch) and the negatively (PPA) charged solutions; after each adsorption step, the excess solution was removed by compressed air (Si wafers) or vigorous squeezing (fabrics). The immersion period for the first couple of layers was set at 5 min; the subsequent layers were obtained after 1 min dipping. The process was repeated until 2 and 4 Bi-Layers (BL) were built on each specimen type. The weight gain on fabrics was around 5 and 7% for 2 and 4 BL, respectively.

Characterization. *Fourier Transformed Infrared Spectroscopy.* The growth of the LbL assembly was monitored using a Frontier FT−IR/FIR spectrophotometer (16 scans and 4 cm^{-1} resolution, PerkinElmer). IR spectra are acquired after each deposition step.

Scanning Electron Microscopy. Si wafer cross sections were imaged using a Field Emission Scanning Electron Microscopy (FESEM) on a ZEISS, FEG MERLIN model.

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

Thermal Stability. 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 (60 mL/min). Ten mg samples were placed in open alumina pans, the experimental error was ±0.5% on weight and ±1 °C on temperature.

Pyrolysis-Combustion-Flow Calorimetry. Pyrolysis-combustion-flow calorimetry (PCFC) was performed on a FAA Micro Calorimeter (Fire Testing Technology). Samples (6.3 ± 0.1 mg) were heated (60 °C/min) in a stream of nitrogen flowing at 80 mL/min. The thermal degradation products from the sample were mixed with a 20 mL/min stream of oxygen and then injected in the combustion furnace (900 °C). Peak Heat Release Rate (PHRR) and Total Heat Release (THR) were measured. The experimental error was ±5%.

Flammability. The flammability of prepared samples has been evaluated in horizontal configuration; the sample (100 × 50 mm^2) was ignited from its short side by a 20 mm methane flame (flame application time: 5 s). The test was repeated at least 3 times for each formulation in order to ensure reproducibility; during the test, parameters such as burning time, afterglow times and final residue were registered.

Cone Calorimetry. Cone calorimetry (Fire Testing Technology, FTT) was employed to investigate the combustion behavior of square samples (100 × 100 mm^2) under 35 kW/m^2 in horizontal configuration, following the ISO 5660 standard. Tests have been performed adopting the optimized procedure for textiles described elsewhere.[47] The following parameters were registered: Time To Ignition (TTI, [s]), peak of Heat Release Rate (pkHRR, [kW/m^2]), Total Heat Release (THR, [MJ/m^2]), carbon dioxide to carbon monoxide ratio (CO_2/CO, [kg/kg]) and final residue.

Fourier Transformed Infrared Spectroscopy in Attenuated Total Reflectance. Attenuated Total Reflectance (ATR) Fourier transformed infrared spectroscopy spectra were collected at room temperature in the range 4000−700 cm^{-1} (16 scans and 4 cm^{-1} resolution) using a Frontier FT−IR/FIR spectroscopy (PerkinElmer, Italy) equipped with a diamond crystal (depth of penetration 1.66 μm, as stated by the Producer).

■ ASSOCIATED CONTENT

ⓈSupporting Information

ATR spectra of neat Starch and PPA, TG, and dTG plots of untreated and LbL treated COT 200 and 400 in nitrogen and air, HRR plots of untreated and LbL treated COT 200 and 400, snapshots of flammability residues and ATR spectra performed on burned region of flammability residues. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b02507.

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Notes

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