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Layer by Layer coatings assembled through dipping, vertical or horizontal spray for cotton flame retardancy

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ABSTRACT

Silica-based assemblies have been deposited on cotton fibres through Layer by Layer technique in order to enhance their flame retardant properties. To this aim, three different deposition procedures (namely, dipping, vertical and horizontal sprays) have been considered and compared. The resulting morphologies of the deposited assemblies have been thoroughly investigated by scanning electron microscopy (SEM) and elemental analysis. SEM observations have demonstrated that only the horizontal spray allows obtaining the deposition of a very homogeneous silica coating when compared to vertical spray or dipping. As a consequence, horizontal spray has proved to ensure the best flame resistance, promoting a substantial increase of the total burning time and final residue, as assessed by flammability tests. Furthermore, cone calorimetry measurements have shown a remarkable increase of the time to ignition, and a significant decrease of heat release rate and total heat release for the fabrics treated by horizontal spray.

1. Introduction

Among the multi-step approaches, the Layer by Layer (LbL) assembly (Decher, 2003) represents an up-to-date technique for the surface modification of different kinds of substrates (plastics, ceramics, metals, wood, fabrics, etc.). LbL was first described in 1966 (Iler, 1966) and has been rediscovered and optimised decades later (Ariga, Hill, & Ji, 2007; Decher, 2003; Decher & Hong, 1991; Hammond, 2004). More specifically, this self-assembly technique has been used to impart barrier properties toward oxygen (Priolo, Gambo, & Grunlan, 2010), anti-reflectivity (Hiller, Mendelsohn, & Rubner, 2002), electrical conductivity (Argun, Ashcraft, & Hammond, 2008; Park, Ham, & Grunlan, 2010; Shim et al., 2007), and antibacterial properties (Dvoracek, Sukhonosova, Benedik, & Grunlan, 2009; Li, Lee, Sheng, Cohen, & Rubner, 2006; Podsiadlo et al., 2005). In its simplest application, LbL method consists in an alternating immersion of the substrate in oppositely charged polyelectrolyte solutions/suspensions, thus building a structure of positively and negatively charged layers piled up on the substrate surface.

Recently, such approach proved to be extremely advantageous when exploited for the flame retardancy of fibres and fabrics. Grunlan and coworkers have demonstrated that LbL can enhance the flame retardancy of cotton, using different organic and inorganic counterparts (Laufer, Carosio, Martinez, Camino, & Grunlan, 2011; Li, Mannen, Schulz, & Grunlan, 2011; Li et al., 2010). Our group has already shown that this assembling strategy allows improving the thermal stability and flame retardancy of polyester by the deposition of nanoarchitectures made either of silica nanoparticles (Carosio, Laufer, Alongi, Camino, & Grunlan, 2011) or α-zirconium phosphate nanoplatelets with different counterparts (i.e. polydiallyldimethylammonium chloride, polyhedral oligomeric silsesquioxanes, or alumina-coated silica nanoparticles, Carosio, Alongi, & Malucelli, 2011).

Very recently, novel systems based on chitosan and ammonium polyphosphate (APP) turned out to be very efficient flame retardants for cotton–polyester blends (Alongi, Carosio, & Malucelli, 2012a; Carosio, Alongi, & Malucelli, 2012). Within these formulations, chitosan acts both as a carbon source and a foaming agent, while APP produces phosphoric acid in situ, favouring the char formation at high temperatures. On the other hand, the silica–APP pair exploits the joint effect of phosphoric acid generated by APP that induces the carbonisation of the polymer, and the thermal insulation behaviour of a ceramer such as silica.

In all the aforementioned papers on the flame retardancy of fibres/fabrics, LbL assembly has been performed by the dipping method: however, spraying could represent an appealing alternative to dipping for its efficiency and feasibility in an industrial scale up, as recently and thoroughly reviewed by Schaaf, Voegel, Jierry, and Boulmedais (2012), who described the basics and application fields of the LbL deposition by vertical spray. The first attempt of spray-assisted LbL has been carried out by Schlenoff, Dubas, and Farhat (2000): LbL films consisting of poly(styrene sulfonate), PSS, and poly(diallyldimethyl ammonium chloride) layers have been

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deposited by dipping or spraying. The results have shown that both the techniques allow achieving the same high uniformity level of the deposited coatings and the same membrane selectivity, as well.

Similar results have been found by Izquierdo, Ono, Voegel, Schaaf, and Decher (2005), who coupled poly(allylamine hydrochloride) with PSS and investigated the efficiency of dipping vs. spraying. Once again, the uniformity and homogeneity of the LbL coatings obtained by vertical spray were comparable with those coming from dipping, with the great additional advantage in the use of spray, i.e. a very short deposition time (3 s).

Although the spray method can also be exploited for covering larger surfaces with respect to dipping, the number of applications of spraying is extremely poor and limited to bioactive materials, surface protection and coatings with enhanced optical properties (Schaaf et al., 2012). To the best authors' knowledge, no study on the use of Layer by Layer spray to impart flame retardancy properties to fibres or fabrics has been published so far. In this respect, the present paper can be considered as a first attempt to reach this goal. Furthermore, a new horizontal spray configuration is presented, that can be extremely effective in limiting the gravity force effect on the spray pattern (i.e. avoid drip patterns in the cascading film), which takes place during vertical spraying, thus leading to the creation of a potential gradient of nanoparticle distribution (Krogman, Zacharia, Schroeder, & Hammond, 2007).

To this aim, silica-based architectures by dipping, vertical or horizontal spray have been deposited on the cotton surfaces to form a Layer by Layer assembly in order to enhance the flame retardant properties of the fabric. The fire performances of the coated cotton fabrics, evaluated through flammability and combustion tests, have been related to the resultant morphologies as assessed by SEM, thus allowing a comparison of efficiency among the above three approaches.

2. Experimental

2.1. Materials

Cotton (COT, 200 g/m^2) was purchased from Fratelli Ballesio S.r.l. (Torino, Italy).

Positive alumina-coated silica (Ludox CL, average diameter: 10 nm, zeta potential: 32.2 mV) and a colloidal suspension of negative silica nanoparticles (Ludox SM30, average diameter: 10 nm, zeta potential: −19.2 mV) were purchased from Sigma Aldrich (Milwaukee, WI) and used as received to prepare the suspensions for LbL assembly. All aqueous suspensions were diluted to 0.2 wt.% using 18.6 MΩ deionised water.

2.2. Layer by Layer–dipping method

Fabric substrates were alternately immersed into the positively and negatively charged silica suspensions in order to build five-fold bilayer architectures. After each immersion step, the substrate was washed with deionised water to remove the excess of ionic species. The immersion period for the first couple of layers was set at 5 min, in order to promote and achieve a uniform deposition; the subsequent layers were obtained after 1 min dipping.

2.3. Layer by Layer–spray methods

Fabric substrates were alternately sprayed with the positively and negatively charged silica suspensions in vertical or horizontal configuration, adopting the same experimental conditions (i.e. time and number of deposited bilayers) as for the dipping process. More specifically, spray nozzles having an i.d. of 500 μm were used, keeping the spray gun at a working distance of 6 cm from the fabric surface.

2.4. Characterization techniques

The surface morphology of the treated samples was studied using a LEO-1450VP Scanning Electron Microscope (beam voltage: 5 kV for the morphological analysis and 20 kV for the elemental analysis); an X-ray probe (INCA Energy Oxford, Cu-Kα X-ray source, k = 1.540562 Å) was used to perform elemental analysis. Fabric pieces (5 mm × 5 mm) were cut and fixed to conductive adhesive tapes and gold-metallized.

The flammability test in vertical configuration was carried out applying a methane flame for 10 s at the bottom of a fabric specimen (50 mm × 150 mm). The test was repeated 5 times for each formulation, measuring burning time and rate, and the final residue, as well.

Cone calorimetry (Fire Testing Technology, FTT) was employed to investigate the combustion behaviour of fabric square samples (100 mm × 100 mm × 0.5 mm) under an irradiative heat flow of 35 kW/m^2 in horizontal configuration, following the procedure described elsewhere (Tata, Alongi, Carosio, & Frache, 2011). The fabrics were placed in a sample holder and maintained in the proper configuration by a metallic grid. time to ignition (TTI, s), total heat release (THR, kW/m^2), heat release rate (HRR, kW/m^2) and the corresponding peak (pkHRR, kW/m^2) were measured. Total smoke release (TSR, m^2/m^2), rate of smoke release (RSR, 1/s), carbon monoxide and dioxide yield ([carbon monoxide] and [carbon dioxide], ppm and %, respectively) were also evaluated. For each sample, the tests were repeated four times in order to ensure reproducible and significant data. The experimental error was within 5%.

3. Results and discussion

3.1. Morphology

SEM observations have been performed in order to assess the morphology of the fibres after the LbL treatments. As is well known, pure cotton fibres are characterised by a level of inhomogeneity due to the natural growing, as evidenced in Fig. 1A. When the fibres are LbL-treated employing the dipping method, their surface becomes rougher (Fig. 1B). The formation of the silica coating on the fibres after dipping has been confirmed by the elemental analysis, which shows a good distribution of Si element (Fig. 2, top line). Indeed, as reported in the literature (Carosio, Laufer, et al., 2011; Laufer et al., 2011), when silica nanoparticles are used for LbL treatments on fabrics, they can promote the formation of an homogeneous coating, the thickness of which is usually below 100 nm, depending on the number of layers deposited. When the fibres are LbL-sprayed, their surface appears completely covered, as well evidenced in Fig. 1C and D. In particular, the horizontal spray (Fig. 1D) seems to be more efficient than the vertical one (Fig. 1C), as the fibres look completely interconnected due to the presence of the coating. In general terms, it is possible to conclude that the horizontal spray allows the formation of a more homogeneous and compact coating on the cotton fibres if compared with the other two deposition methods. The elemental analysis, as depicted in Fig. 2, seems to indicate a higher Si content for the sample treated with the horizontal spray (bottom line) with respect to the fabrics treated with the other LbL deposition methods (top and medium lines). Although the EDS investigation allows only a semi-quantitative analysis, by employing a high beam voltage (i.e. 20 kV) it is possible to exploit the high penetration of the incident beam to discriminate among the depositions obtained by the three different procedures. Therefore, we have tried to evaluate the Si amount present on the samples, which

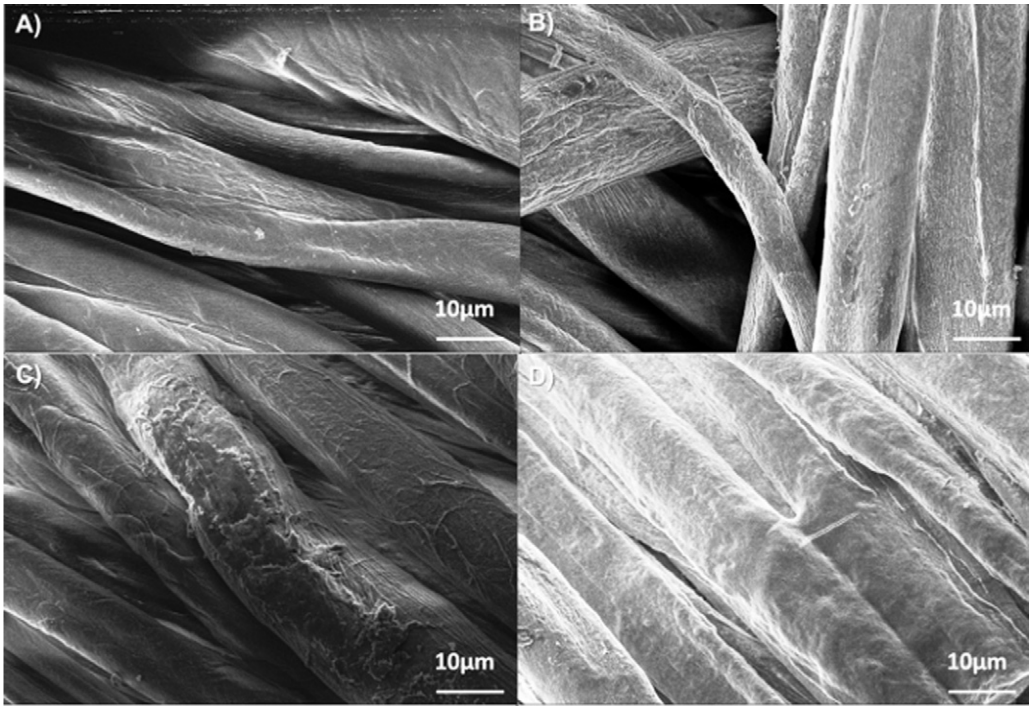

Fig. 1. SEM micrographs of cotton fabrics: neat (A) and LbL-treated by dipping (B), vertical (C) and horizontal spray (D).

has been found equal to 3.1 ± 0.1 (horizontal spray), 0.9 ± 0.1 (vertical spray) and 0.5 ± 0.1 wt.% (dipping). These data clearly indicate that only the horizontal spray can achieve a more homogeneous and consistent coverage of the fibres.

These findings could also be put in relation to a particular phenomenon, which occurs only during the dipping procedure, when the rinsing solution is replaced by that containing the oppositely charged solution/suspension: indeed, the formation of a zone, close to the substrate surface, characterised by a very low (poly)electrolyte concentration (the so-called *depletion zone*) occurs (Izquierdo et al., 2005; Porcel et al., 2005). As a consequence, the layer components have to diffuse through this depletion zone before reaching the surface of the fabric, thus taking more time for achieving a good level of homogeneity of the LbL assembly, with respect to the two spray methods.

The morphological differences observed on the three samples by SEM can significantly affect the obtained flame retardancy properties, as already reported in the literature for cotton–polyester

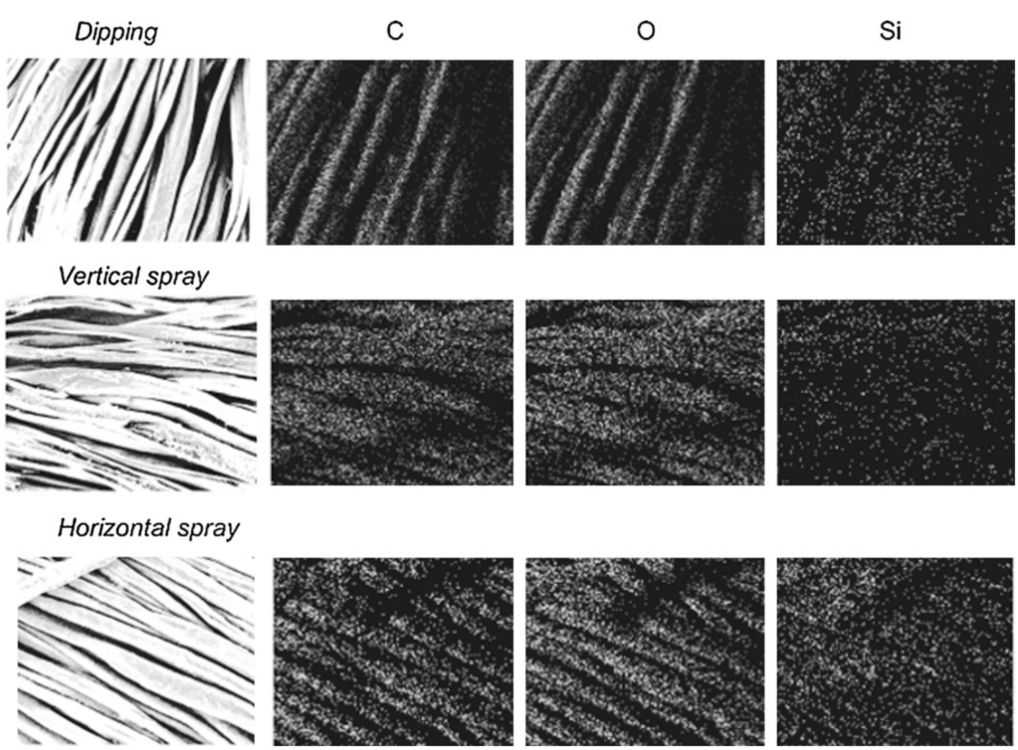

Fig. 2. EDS mapping of cotton fabrics LbL-treated by dipping, vertical and horizontal spray.

Table 1
Cone calorimetry data of neat and LbL-treated fabrics.

Sample	TTI [s]	THR [MJ/m^2]	pkHRR [kW/m^2]	TSR[a] [m^2/m^2]	RSR		Residue [g]
					Peak [1/s]	Time [s]	
COT	22	2.0	83	4.3	1.1	30	0.01
COT_silica_dipping	20	2.2	75	2.9	0.8	28	0.03
COT_silica_vertical spray	20	2.2	73	2.5	0.8	34	0.04
COT_silica_horizontal spray	28	2.0	66	3.6	0.9	36	0.04

[a] Evaluated at TTI.

blends LbL-treated with ammonium polyphosphate and other components by dipping (Alongi et al., 2012a; Alongi, Carosio, & Malucelli, 2012b; Carosio et al., 2012) and will be discussed in the following paragraphs.

3.2. Combustion behaviour

The flame retardancy properties of the LbL-treated samples in terms of resistance to an irradiating heat flow have been assessed by cone calorimetry. The collected data are listed in Table 1 in terms of TTI, THR, pkHRR, TSR and its rate, RSR and residue, and plotted in Fig. 3, as HRR and THR vs. time.

When the silica coating is applied by dipping or vertical spraying on the cotton fibres, the time to ignition (TTI) does not change (its variation is within the experimental error), while the heat release rate and corresponding peak are slightly reduced (*see* pkHRR, Table 1). On the contrary, when the fabrics are horizontally sprayed, a significant TTI increase (28 s vs. 20 s) and pkHRR decrease (66 kW/m^2 vs. 83 kW/m^2) are registered (Fig. 3A and Table 1). This finding is in agreement with the THR curve that shifts toward longer times for the horizontally sprayed fabrics, unlike all the other samples including neat cotton (Fig. 3B). This behaviour is entirely attributable to the morphology of the coating observed by SEM (Fig. 1) and to the Si amount found by the elemental analysis (Fig. 2). Indeed, the horizontal spray has proven to be the most efficient deposition procedure in terms of consistent and homogeneous coating deposited on the cotton fibres.

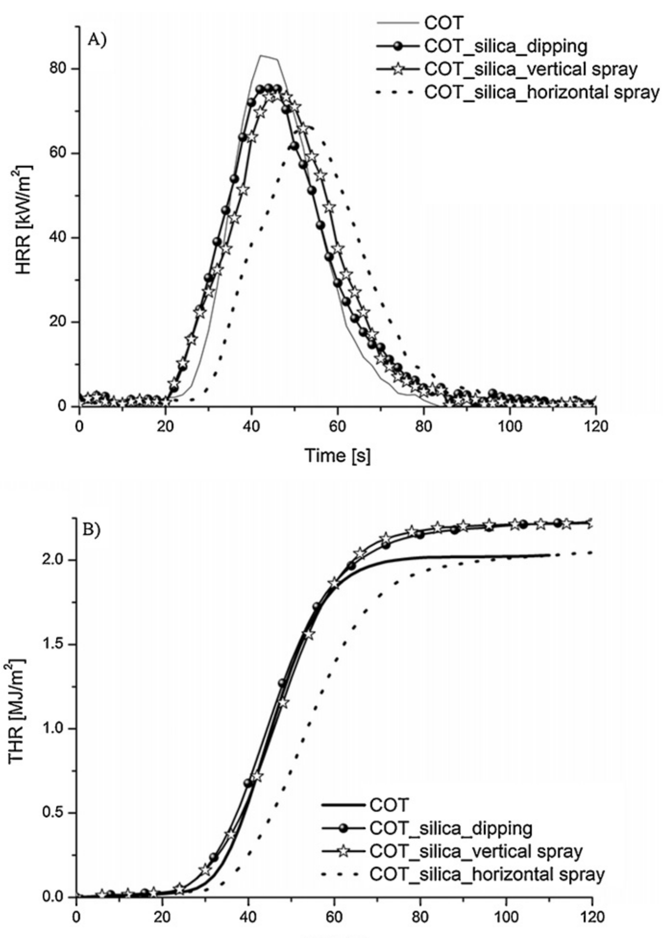

Fig. 3. HRR and THR curves of neat and LbL-treated fabrics.

As far as smoke production is concerned, a significant TSR reduction for all the LbL-treated samples has been observed (Table 1 and Fig. 4A): this behaviour can be ascribed to the specific silica behaviour as smoke suppressant, as already reported in the literature (Alongi & Malucelli, 2012). Indeed, silica has proven to be an inert filler able to reduce the amount of smokes generated from a given polymer mass (or volume) by simply diluting or decreasing the amount of combustible substrate available and also by absorbing heat, so that the burning rate slows down. Despite this “physical” protection, a catalytic effect exerted by the nanofiller cannot be neglected: indeed, alumina-coated silica may help the acid-catalysed dehydration of the fibres and, as a result, can enhance the char formation (Carosio, Alongi, et al., 2011; Lewin & Weil, 2001). More specifically, the horizontal spray is capable to postpone the production of smokes since it delays the ignition, as observable by the shift of the TSR curve (Fig. 4A). Furthermore, the smoke production rate (measured as RSR) is somehow decreased and shifted in time, as well (Fig. 4B and Table 1). The silica coating is also responsible for a drastic reduction of the CO_2 production, while the CO amount remains almost unchanged (Fig. 4C and D).

At the end of the cone calorimetry test, some residue of the LbL-treated sample is still present (Table 1); the SEM magnifications reported in Fig. 5 show that the fibres maintain the original texture after the combustion (1st row) and still consist of C, O and Si the final residue mainly consists of C, O and Si elements (2nd, 3rd and 4th row). This finding demonstrates that the coating is able to partially protect the cotton fibres during the combustion, inhibiting the production of volatiles and favouring the formation of a carbonaceous structure (*char*). Indeed (Fig. 5).

3.3. Flammability

Flammability tests have been carried out on the neat and LbL-treated cotton fabrics by applying a methane flame to the specimens. The data summarised in Table 2 show that the coating deposited by dipping is not able to reduce the flammability of cotton: indeed, burning time and rate do not substantially change. On the contrary, vertical and horizontal sprays are

Table 2
Flammability data of neat and LbL-treated fabrics.

Sample	Burning time [s]	Burning rate [mm/s]	Residue [%]
COT	20	7.5	–
COT_silica_dipping	22	6.8	2
COT_silica_vertical spray	30	5.0	3
COT_silica_horizontal spray	30	5.0	5

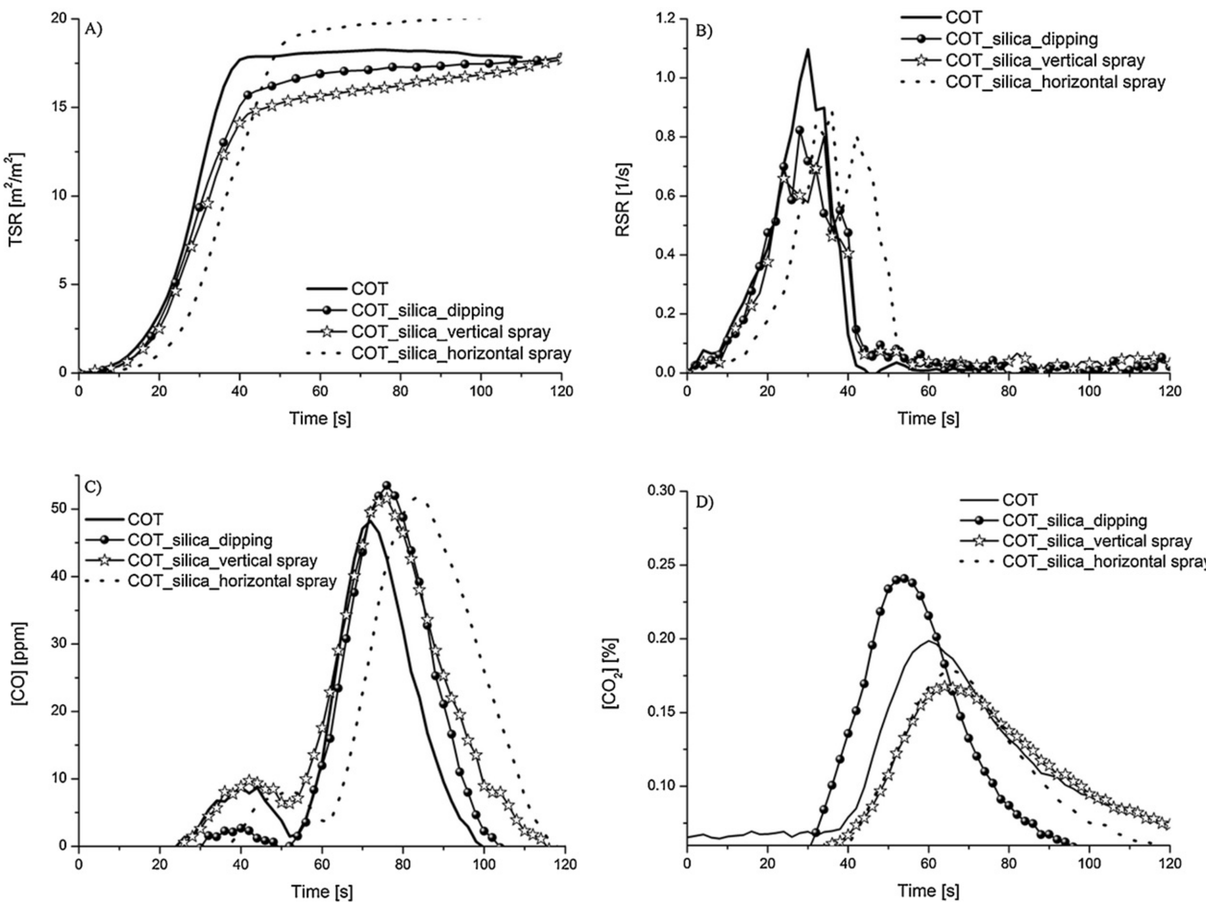

Fig. 4. TSR, RSR, CO and CO_2 curves of neat and LbL-treated fabrics.

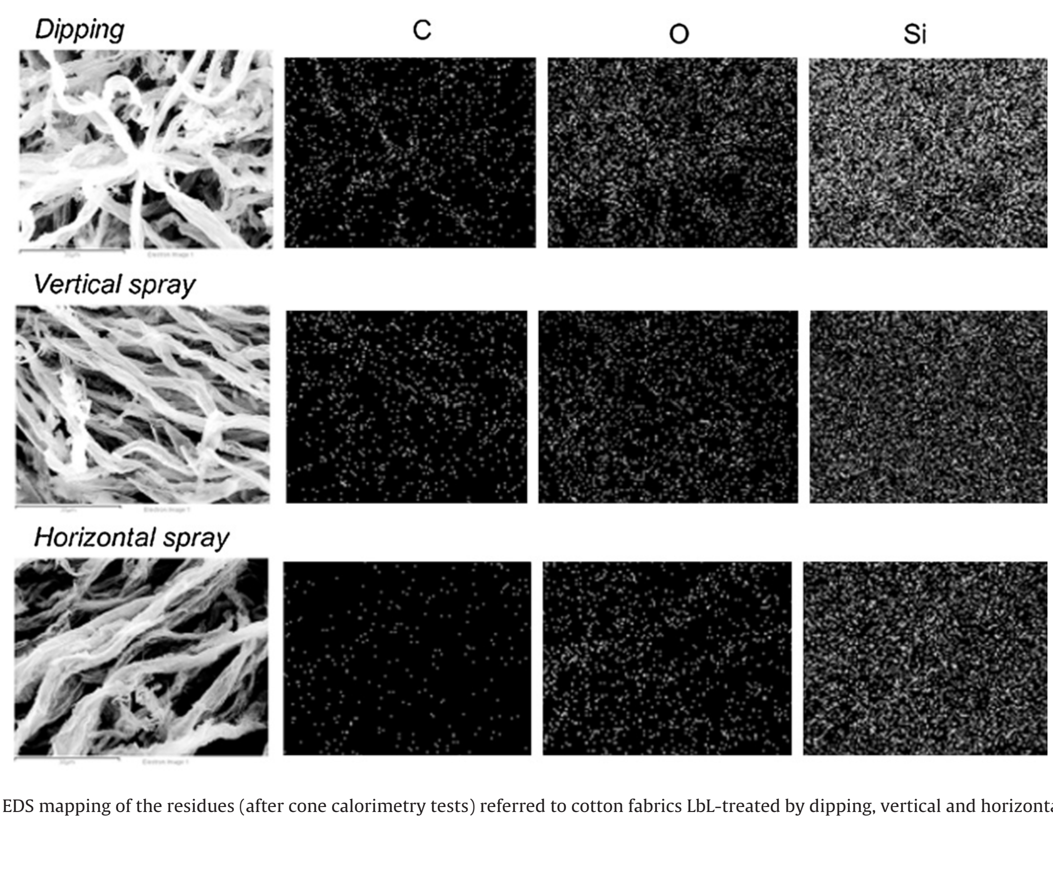

Fig. 5. EDS mapping of the residues (after cone calorimetry tests) referred to cotton fabrics LbL-treated by dipping, vertical and horizontal spray.

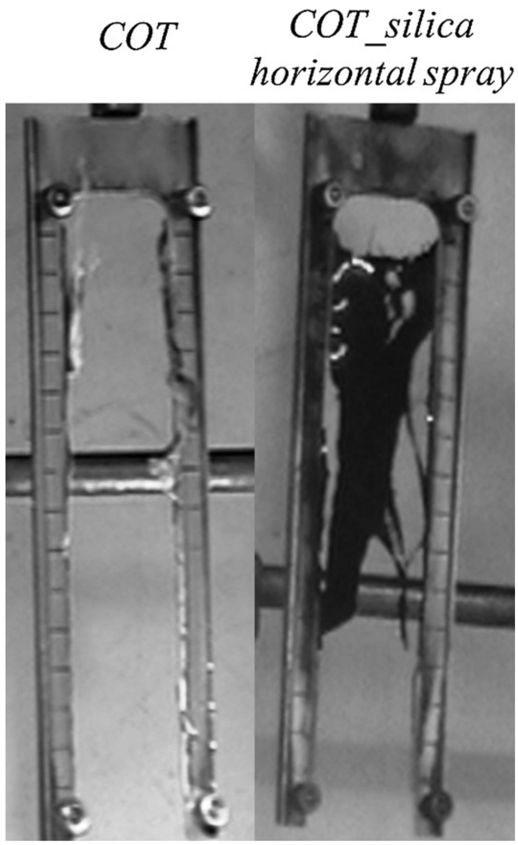

Fig. 6. Fabric residues after flammability tests.

capable to significantly increase the total burning time and reduce the burning rate, promoting the formation of a carbonaceous residue, as evidenced in Fig. 6 for the neat and LbL-horizontally sprayed cotton specimens.

4. Conclusions

In the present work, silica bilayer-based coatings have been deposited on cotton fibres by Layer by Layer assembly, employing three different deposition procedures (i.e. dipping, vertical and horizontal spray). The effectiveness of each deposition method for homogeneously covering the cotton fibres has been assessed and the relationship between the obtained morphologies and the resulting flame retardancy properties thoroughly investigated. In particular, SEM observations have shown that the most homogeneous and consistent depositions have been achieved by using the horizontal spray, which has proven to confer the best flame retardancy properties. Indeed, with respect to vertical spraying, this configuration can be extremely effective in avoiding drip patterns in the cascading film, thus leading to the formation of a homogeneous and compact silica coating.

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