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Cotton fabrics treated with novel oxidic phases acting as effective smoke suppressants

Jenny Alongi*, Giulio Malucelli

Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Viale Teresa Michel 5, 15121 Alessandria, Italy

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A B S T R A C T

Sol–gel processes have been applied to cotton fabrics in order to coat the fibres with a silica film, able to improve their thermo-oxidative resistance and their combustion behaviour under the irradiative heat flow of a cone calorimeter. To this aim, tetramethoxysilane, inorganic precursor of the silica phase, has been employed alone or coupled with species having either smoke suppressant features (namely, zinc oxide, zinc acetate dihydrate and zinc borate) or well known flame retardant properties (like ammonium pentaborate octahydrate, boron phosphate, ammonium polyphosphate and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide). In addition, the use of barium sulphate, which is a smoke suppressant and, at the same time, a flame retardant, has been investigated. Cone calorimetry turned out to be a suitable technique for assessing the flammability and smoke production of the treated fabrics (particularly when referring to total smoke release, smoke production rate and CO and CO_2 yields). The composition and morphology of the deposited coatings, assessed by scanning electron microscopy, have been found to influence their combustion behaviour, as well as their thermal and thermo-oxidative stability evaluated by thermogravimetric analysis in nitrogen and air, respectively.

1. Introduction

Smoke has a vague definition, as addressed by Price, Anthony, and Carty (2001): indeed, it is generally considered to be a cloud of particles (individually invisible because of their reduced size), able to scatter and/or absorb visible light. Smoke differs from *fume*, since this latter can be considered as a less opaque form of smoke. During the combustion of a polymer, the production of “combustible gases” (i.e. CO) and “visible smokes” are crucial factors to take in consideration since the loss of visibility due to heavy smoke can hinder escape pathways, while toxic gas concentration (especially at high temperatures) can be very critical. Most likely, since escape time can get benefits from the reduction of the rate and intensity of visible smoke development, the investigation on effective smoke suppressants for polymers becomes a key parameter in the combustion processes of the latter. Visible smoke from burning polymers is usually a consequence of incomplete combustion. Upon heating, at certain temperatures, polymers undergo pyrolysis, thus giving rise to low molecular weight species (Price et al., 2001). These species diffuse from the solid into the gas phase, where they form smoke and other reactive species that further fuel the polymer combustion. Namely, aliphatic species are cracked to small alkyl radicals and grow to form conjugated polyenes or polybenzenoids that react and condense with other unsaturated species to give soot. Meanwhile, the oxidation of carbon to oxides (CO and CO_2) occurs through a competitive pathway to the soot formation. Indeed, the mechanism by which a polymer burns is very complex and the number of the involved parameters is high. Several approaches, that involve certain chemical reactions occurring either in gas phase or in solid and liquid phases, have been developed for reducing the smoke production. The chemical reactions taking place in the solid phase seem to be one of the most promising and encouraging routes, as they allow diluting the combustible polymer content, dissipating heat, insulating and protecting the surface of the combustible substrate and finally promoting the formation of char and modifying the pyrolysis reactions.

Within the above scenario, all the flame retardant systems adopted for natural fibres (such as cotton or viscose) derive from a chemical finishing process, which is able to enhance the flame retardant efficiency and the durability to laundering, according to the chemical nature and cost of the flame retardant itself. These systems may simply consist of soluble salts (i.e. ammonium phosphate and polyphosphate, borate–boric acid mixtures), which can be exploited for non-durable finishes. In some other cases, they may be chemically reactive (i.e. alkylphosphonamide derivatives and tetrakis hydroxylmethylphosphonium salts), thus providing functional finishes for durable flame retardancy; finally, they can

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* Corresponding author. Tel.: +39 0131229337; fax: +39 0131229399.
E-mail address: jenny.alongi@polito.it (J. Alongi).

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be utilized as back coatings, which usually comprise a resin-bonded antimony/bromine flame retardant system (Horrocks, 1986, 2001, 2008, 2011; Horrocks, Kandola, Davies, Zhang, & Padbury, 2005). It should be noted that, since the most effective flame retardants contain either phosphorus- or antimony/bromine-based compounds, they generate a perception of unacceptable environmental hazard. Indeed, their use may result in significant effects on toxic potency by modifying combustion efficiency and increasing the yields of smoke and asphyxiant gases. As an example, cotton treated with a bromine/antimony back coating is able to produce a higher amount of carbon monoxide (by a factor of 10) with respect to the untreated fabric in non-flaming conditions at 700 °C (Purser, 2001).

For these reasons, the requirement of safety and eco-friendly systems acting as smoke suppressants or flame retardants or having both the above features is continuously growing. The latter solution seems to be the most promising and appreciable from an economical point of view. Antimony, iron, molybdenum and zinc compounds represent the most promising and efficient systems (Price et al., 2001). On one hand, the use of fillers, classified as *inert* or *active*, on the basis of their apparent smoke suppressant functions, is already documented in the literature for bulk polymers. Such inert fillers as silica, clays and calcium carbonate are able to lower the amount of smoke generated from a given mass or volume of a polymer, by simply diluting or decreasing the amount of combustible substrate present and also by absorbing heat (so that the burning rate slows down). On the other hand, aluminium and magnesium hydroxides behave as active fillers: they differ from the inert counterpart since they give rise to endothermic processes, which are capable to absorb more heat per unit weight, being equal the diluent and heat adsorption functions.

Referring to inert fillers, silica nanoparticles or silica-based coatings can be easily synthesized through sol–gel processes: as clearly reported in the literature, these latter represent a versatile synthetic route based on a two-step reaction (hydrolysis and condensation), starting from (semi)metal alkoxides (tetraethoxysilane, tetramethoxysilane, titanium tetraisopropoxide, etc.), that leads to the formation of completely inorganic or hybrid organic–inorganic coatings at or near room temperature (Sakka, 2003). Recently, our group has demonstrated that sol–gel treatments are able to modify the combustion behaviour of cotton fabrics forming a silica coating able to act as a surface thermal insulator, diluting the combustible polymer content, dissipating heat, hindering the formation of volatile species that fuel further degradation and favouring the formation of char (Alongi, Ciobanu, Carosio, Tata, & Malucelli, 2011; Alongi, Ciobanu, & Malucelli, 2011a, 2011b, 2011c; Alongi, Ciobanu, & Malucelli, 2012a, 2012b, in press).

In the present work, the effect of silica alone or coupled with other active species acting as smoke suppressants on the flammability and smoke production for cotton fabrics has been thoroughly explored. More specifically, the joint effect between silica and tin-, boron- or phosphorus-based compounds has been pursued and assessed. Among these species, only tin-based compounds are classifiable as smoke suppressants (Horrocks, Smart, Nazaré, Kandola, & Price, 2010; Kandare, Kandola, Price, Nazaré, & Horrocks, 2008; Nazaré, Kandola, & Horrocks, 2008; Price et al., 2001), while the other compounds are known for their flame retardant features. In addition, the investigation has been extended to barium sulphate, which exhibits both the characteristics. A deep investigation on the total smoke release, the smoke production rate, and CO and CO_2 yields has been performed by cone calorimetry, in order to evaluate the effect of each type of additive on the smoke production. The obtained results have been related to the morphology of the deposited coatings (assessed by scanning electron microscopy) as well as their thermal stability in inert and oxidative atmosphere (evaluated by thermogravimetric analysis in nitrogen and air, respectively).

2. Experimental

2.1. Materials

Cotton fabrics (CO, purchased from Fratelli Ballesio, Torino, Italy) with a density of 290 g/m^2 were used as received.

Tetramethylorthosilicate (TMOS), water, ethanol, dibutyltindiacetate (DBTA, condensation catalyst), smoke suppressants (namely, zinc oxide – ZnO, zinc acetate dehydrate – ZnAc and zinc borate – ZnB), flame retardants (namely, ammonium pentaborate octahydrate – APB, boron phosphate – BP, ammonium polyphosphate – APP and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide – DOPO), all reagent grades, were purchased from Sigma–Aldrich and used without any further purification. Barium sulphate (BaS) was purchased from Sigma–Aldrich and used without any further purification both as smoke suppressant and flame retardant.

2.2. Sol–gel treatments performed on cotton

First of all, pure silica phases were obtained from a sol containing tetramethylorthosilicate, distilled water (precursor:water molar ratio = 1:1), ethanol and DBTA (0.9 wt.%); the cotton fabrics were impregnated in the sol solution for 5 min at r.t. and subsequently thermally treated at 80 °C for 15 h using a gravity convection oven.

In addition, in some formulations smoke suppressants or flame retardants were also added to the sol solution (according to their solubility) before adding DBTA (condensation catalyst). All the formulations identified with a sample code CO_Si or CO_Si_X are collected in Table 1.

The add-on of total dry solids on cotton samples (*A*, wt.%) was determined by weighting each sample before (W_i) and after the impregnation with the sol solution and the subsequent thermal treatment (W_f), using a Sartorius balance ($\pm 10^{-4}$ g). The precursor uptake (reported in Table 1) was calculated according to the following equation:

$$A = \frac{W_f - W_i}{W_i} 100$$

2.3. Characterization techniques

The surface morphology of the treated samples was studied using a LEO-1450VP Scanning Electron Microscope (beam voltage: 20 kV), equipped with a X-ray probe (INCA Energy Oxford, Cu-Kα X-ray source, $k = 1.540562$ Å), which was used to perform elemental analysis. Fabric pieces (5 mm × 5 mm) 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.

The combustion behaviour of square fabric samples (100 mm × 100 mm × 0.5 mm) was investigated using cone calorimetry (Fire Testing Technology, FTT). The measurements were carried out under a 35 kW/m^2 irradiative heat flow in horizontal configuration, following the procedure described elsewhere (Tata, Alongi, Carosio, & Frache, 2011). Such parameters as Time To Ignition (TTI, s), Total Heat Release (THR, kW/m^2), peak of Heat Release Rate (HRR, kW/m^2) were measured. Total Smoke Release (TSR, m^2/m^2), peak of Rate of Smoke Release (1/s), Smoke Factor (SF, calculated as PHRR × TSR, MW/m^2) and CO and CO_2 release (g/s) were evaluated, as well. The experiments were repeated four times for each material investigated to ensure reproducible

Table 1
Formulations investigated.

Sample code	Flame retardant	Flame retardant type	Flame retardant content [g]	Add on [%]
CO_Si	–	–	–	19
CO_Si_ZnO	Zinc oxide	Smoke suppressant	0.50	38
CO_Si_ZnAc	Zinc acetate dihydrate	Smoke suppressant	1.05	34
CO_Si_ZnB	Zinc borate	Smoke suppressant + flame retardant + after glow suppressant	1.00	38
CO_Si_APB	Ammonium pentaborate octahydrate	Inorganic blowing agent and glass-forming flame retardant	0.50	28
CO_Si_BP	Boron phosphate	Flame retardant acting in condensed phase	0.51	34
CO_Si_APP	Ammonium polyphosphate	Flame retardant acting in condensed phase	0.54	42
CO_Si_DOPO	9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide	Flame retardant acting both in vapour and condensed phase	0.50	25
CO_Si_BaS	Barium sulphate	Smoke suppressant + flame retardant acting in condensed phase	0.57	28

and significant data; the experimental error was within 2%. Prior to flammability and combustion tests, all the specimens were conditioned at 23 ± 1 °C, 50% R.H. in a climatic chamber for 48 h.

3. Results and discussion

3.1. Morphology

In order to assess the morphology of the coatings deposited on cotton fibres by sol–gel processes, SEM observations have been performed. The typical morphology of cotton fibres is reported in Fig. 1A and B: as expected, the surface of raw cotton fibres shows a certain level of irregularity, which disappears when the fibres are sol–gel treated. Indeed, all the treated fibres usually appear homogeneously covered by a continuous thin film consisting of the silica phase, even in the presence of smoke suppressant or flame retardant species: as an example, two SEM micrographs of CO_Si are reported in Fig. 1C and D, respectively. Only CO_Si_ZnB and CO_Si_BaS have shown a different morphology: the presence of microaggregates dispersed in the film is evident in Fig. 2A and C, where two SEM micrographs of CO_Si_ZnB and CO_Si_BaS are reported, respectively. The chemical composition of such aggregates has been assessed by elemental analysis: they contain Zn and B elements for the former sample (Fig. 2B) and Ba and S elements for the latter sample (Fig. 2D), apart from C, O and Si (ascribed to cotton fibres and silica coating).

3.2. Thermal stability

The thermal and thermo-oxidative stability of pure and treated cotton fabrics have been evaluated by thermogravimetric analyses in inert and oxidative atmosphere, respectively. Tables 2 and 3 summarise the collected data in nitrogen and air, respectively.

As already assessed (Alongi, Ciobanu, et al., 2011; Alongi et al., 2011a, 2011b, 2011c; Alongi et al., 2012a, 2012b, in press), the thermal degradation of cotton in nitrogen proceeds by a single step, during which the maximum weight loss is registered (Fig. 3A, full line). Indeed, cotton usually pyrolyzes in nitrogen according to two alternative pathways, which involve the decomposition of the glycosyl units to char at lower temperatures and the depolymerization of such units to volatile products containing levoglucosan at higher temperature.

The presence of silica coating is responsible of a strong anticipation of cellulose decomposition (Table 2), as revealed by the $T_{onset5\%}$ value (235 vs. 290 °C for CO_Si and CO, respectively) and the corresponding time (18.91 vs. 24.43 min), well depicted by TG and dTG curves (Fig. 3A, full points). This behaviour is still maintained in the presence of either the smoke suppressants or flame retardants in the sol solution during the coating preparation (Fig. 3B–D), with the only exception of BP- and APP-containing samples: indeed, BP and APP are able to delay the cellulose decomposition (302 vs. 290 °C for both CO_Si_BP and CO_Si_APP vs. CO, respectively). As a matter of fact, at ca. 280 °C, APP starts to decompose into liquid polyphosphoric acids that phosphorylate the cellulose, favouring its dehydration and char formation reactions. It has already been observed that the thermal decomposition of APP is sensitised by the presence of metal ions. Indeed, preliminary studies carried out by Davies, Horrocks, and Alderson (2005) have shown that metal ion-doped APP in the presence of cellulose not only promotes a further sensitisation of cellulose decomposition but also improves its flame retardancy (assessed by limiting oxygen index, LOI, measurements), when APP is applied as a back-coating to cotton fabric. Hence, the joined effect of APP and Si promotes the delay of the cellulose decomposition. Referring to BP, a similar behaviour can be foreseen, taking in account the results by Shaw and co-workers for polyamide 6 loaded with boron phosphate and silicon oil (Shaw, 1998).

At higher temperatures, namely at T_{onset} (defined as change of slope) and $T_{10\%}$ weight loss, all the coatings are able to postpone the cellulose decomposition (see also corresponding times in Table 2) since the silica coating acts as a thermal insulator protecting the cotton from its thermal decomposition. Once again, the joint effect between silica coating and phosphorus-based compounds is observed.

At the maximum weight loss, any coating under study slightly anticipates the cellulose decomposition, but at the same time a higher residue is formed if compared with that left by pure cotton (see T_{max}, t and residues in Table 2). The silica coating, acting as an inert filler, promotes the char formation by converting the organic fibre structure to a carbonaceous residue and hence reducing volatiles (i.e. fuel) formation. In addition, the char behaves as a carbonised replica of the original fabric and continues to assure a thermal barrier. By this way, the residue of CO_Si is higher than that of cotton (59.6 vs. 42.3%).

When ZnO, ZnAc or ZnB are added to the sol solution, a joint effect between zinc and silica is observed, as evidenced by their residues (68.2, 60.2 and 62.2%, Fig. 3B). In particular, it is noteworthy that ZnO gives the best results in comparison with the homologue species, probably because of its complete solubility in the sol solution that allows the formation of a homogeneous coating, unlike ZnB that tends to form microaggregates (see aforementioned SEM micrographs of Fig. 2A and B). Among the flame retardant species, the highest residues at the maximum weight loss have been found for BP and APP (69.3 and 69.0%, respectively, in Table 2 and Fig. 3C and D). Such residues probably consist of a strong

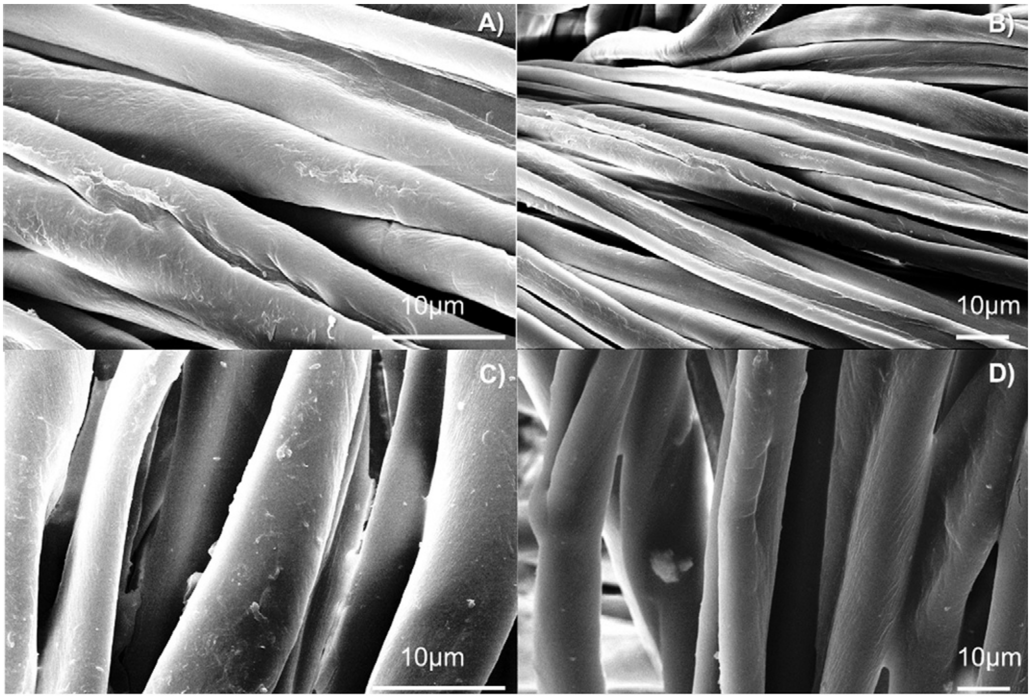

Fig. 1. SEM magnifications of untreated cotton (A and B) and fabrics treated with silica alone (C and D).

and coherent char that is thermally stable up to ca. 700 °C: indeed, their T_{endpoint} values (720 and 696 °C for CO_Si_BP and CO_Si_APP, respectively) and the corresponding residues (40.8 and 41.8%) are the highest with respect to any other coating (Table 2).

Generally speaking, it is interesting to observe that all the coatings deposited on cotton fabrics are able to delay cellulose decomposition in a remarkable way.

As far as the thermo-oxidative stability is considered, cotton degradation usually occurs in three steps, as schematized in Fig. 4. The first step (300–400 °C) involves two competitive pathways, which yield aliphatic char and volatile products; during the second step (400–600 °C) a fraction of the aliphatic char converts to an aromatic form, yielding CO, CO_2, methane and water as a consequence of simultaneous carbonization and char

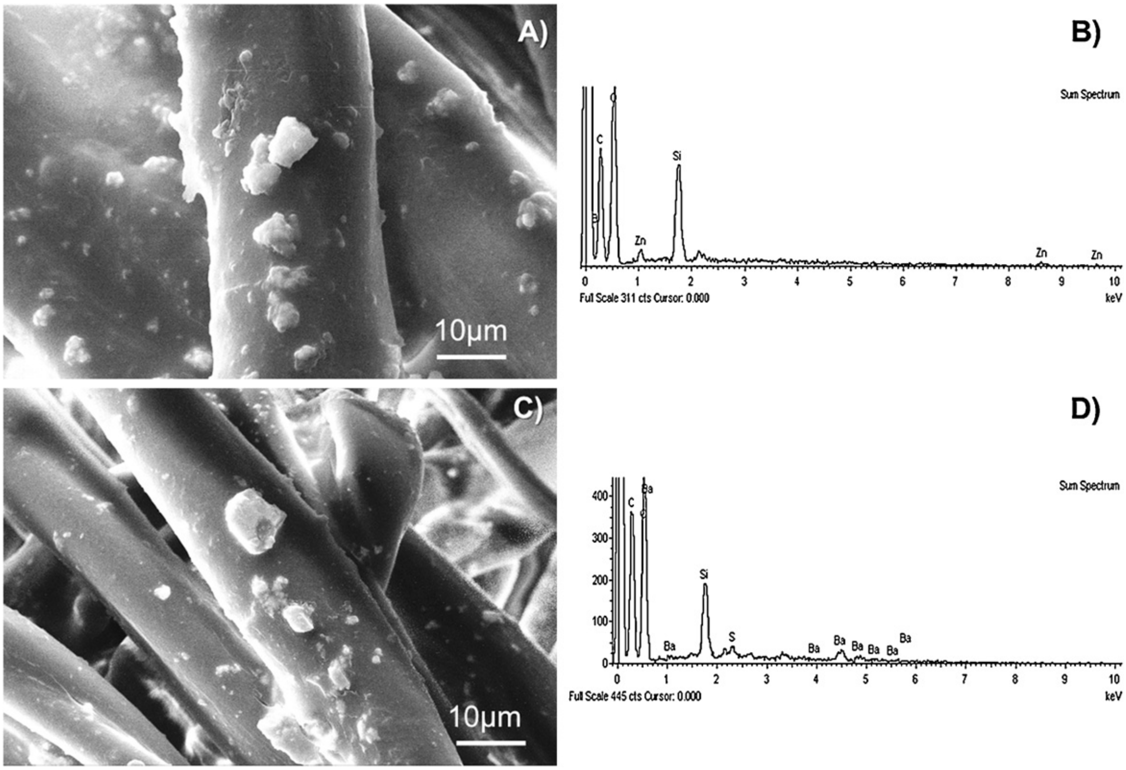

Fig. 2. SEM magnifications of fabrics treated with silica + ZnB (A) and silica + BaS (B) and corresponding elemental analyses (C and D).

Table 2
TGA data in nitrogen.

Sample	5% Weight loss		Onset of weight loss		10% Weight loss		Maximum weight loss			Endpoint of weight loss		
	T [°C]	t [min]	T [°C]	t [min]	T [°C]	t [min]	T_{max} [°C]	t [min]	Residue [%]	T [°C]	t [min]	Residue [%]
CO	290	24.43	300	25.46	316	26.54	366	32.07	42.3	602	55.66	13.4
CO_Si	235	18.91	304	25.82	322	27.63	362	31.61	59.6	652	60.67	34.0
CO_Si_ZnO	232	18.61	315	26.99	333	28.79	356	31.23	68.2	673	62.73	38.7
CO_Si_ZnAc	274	22.91	315	26.99	332	28.66	356	31.05	60.2	644	59.82	30.7
CO_Si_ZnB	251	20.60	313	26.82	335	28.95	359	31.35	62.2	638	59.25	34.8
CO_Si_APB	178	13.24	314	26.87	324	27.84	349	30.35	62.3	650	60.42	35.5
CO_Si_BP	302	25.72	326	28.10	339	29.40	358	31.30	69.3	720	67.45	40.8
CO_Si_APP	302	25.64	324	27.92	339	29.42	358	31.25	69.0	696	65.06	41.8
CO_Si_DOPO	267	22.22	318	27.31	328	28.27	358	31.27	57.6	660	61.44	31.9
CO_Si_BaS	242	19.68	317	27.18	334	28.90	361	31.58	62.9	637	59.14	37.0

oxidation. At the same time, volatile species evolve again in CO, CO_2, methane and water. In the last step (800–900 °C), the char (and any remaining hydrocarbon species) are further oxidized mainly to CO and CO_2 (Horrocks, 2001; Price, Horrocks, Akalin, & Faroq, 1997).

In the present work, two decomposition peaks are observable in the range between 300 and 500 °C for cotton (namely at 344 and 485 °C, Table 3 and TG and dTG curves in Fig. 5A). Once again, the presence of the silica coating induces a strong anticipation of T at 5% of weight loss, a significant delay of T at 10% of weight loss and T_{onset} (123, 306, and 317 vs. 262, 285 and 309 for CO_Si and CO, respectively). The first maximum weight loss (T_{max1}) remains constant, whereas the second (T_{max2}) is postponed. The residue formed during this second step is a thermally stable char that evolves at high temperatures, leaving a residue significantly higher with respect to that of pure cotton (19.8 vs. 1.4%). As already observed in nitrogen atmosphere, every coating is able to protect the fabrics from their thermo-oxidation, exploiting a joint effect of silica

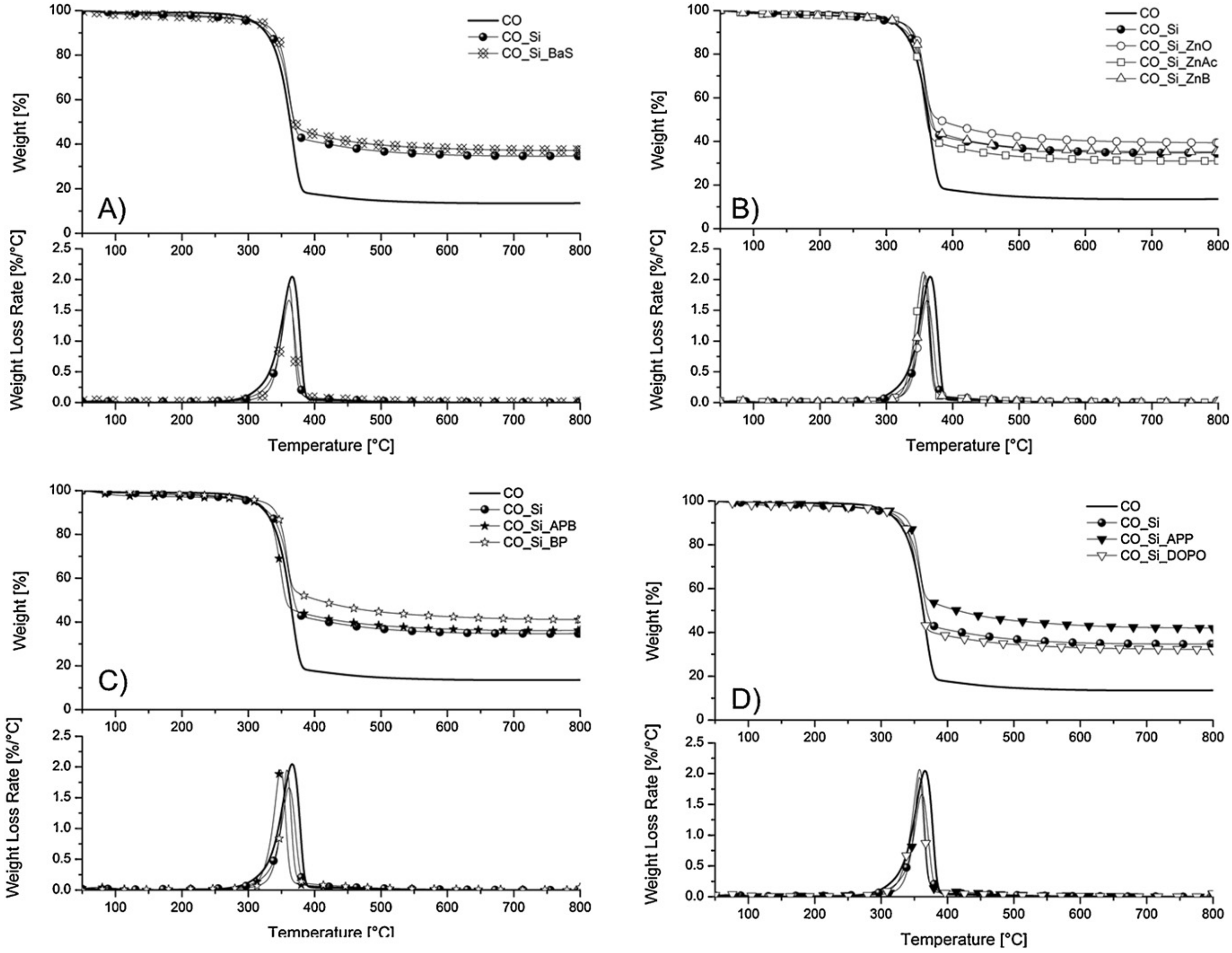

Fig. 3. TG and dTG curves of untreated and sol–gel treated cotton fabrics in nitrogen.

Table 3
TGA data in air.

Sample	5% Weight loss		Onset of weight loss		10% Weight loss		1st Maximum weight loss			2nd Maximum weight loss			Endpoint of weight loss		
	T [°C]	t [min]	T [°C]	t [min]	T [°C]	t [min]	$T_{\max1}$ [°C]	t [min]	Residue [%]	$T_{\max2}$ [°C]	t [min]	Residue [%]	T [°C]	t [min]	Residue [%]
CO	262	21.62	285	20.97	309	26.41	344	29.89	50.0	485	44.00	5.0	491	44.60	1.4
CO_Si	123	7.72	306	24.15	317	27.16	343	29.75	62.6	499	45.40	25.7	560	51.41	19.8
CO_Si_ZnO	284	23.87	306	26.03	328	28.28	346	30.08	65.0	492	44.60	31.2	586	54.05	26.0
CO_Si_ZnAc	193	14.75	306	26.02	315	27.00	345	29.99	58.9	498	45.22	23.5	591	54.51	18.5
CO_Si_ZnB	178	13.29	303	25.13	322	27.70	346	30.11	63.8	503	45.79	28.9	584	53.87	23.3
CO_Si_APB	101	5.54	307	26.17	319	27.34	341	29.38	65.7	501	45.53	31.5	600	55.47	26.0
CO_Si_BP	289	24.4	321	27.60	330	30.37	349	28.51	65.3	505	46.00	30.3	613	56.71	24.0
CO_Si_APP	289	24.4	314	26.90	329	28.36	347	30.20	65.8	498	45.29	30.6	591	54.59	24.1
CO_Si_DOPO	219	17.4	302	25.70	321	27.58	343	29.79	63.8	500	45.50	28.6	589	54.30	23.2
CO_Si_BaS	206	16.08	304	25.93	322	27.71	346	30.08	63.1	505	45.97	29.2	586	58.51	24.0

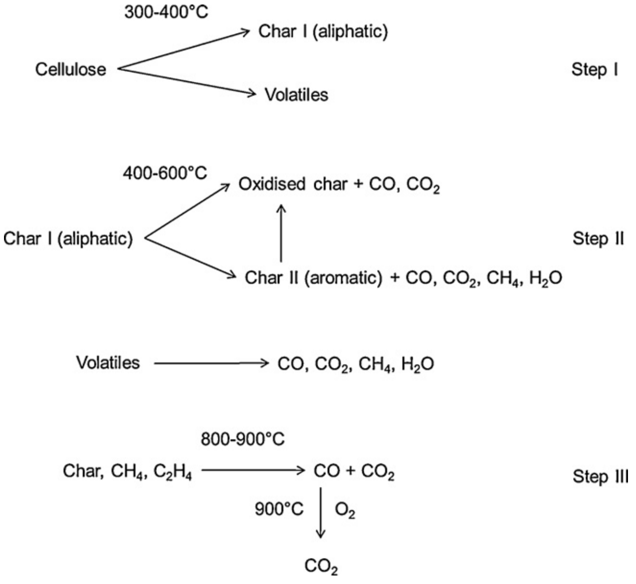

Fig. 4. Scheme of the cellulose degradation and char formation (Horrocks, 2001).

and smoke suppressant or flame retardant species (Fig. 5B–D): this is confirmed by the T_{onset}, $T_{10\%}$, $T_{\max2}$, T_{endpoint} values and final residues of these samples, as compared to CO_Si (Table 3). The best results have been achieved using ZnO, APB, BP, APP and BaS. As far as ZnO, BP and APP are considered, their mechanism has been explained above. On the other hand, APB (ammonium pentaborate octahydrate) leaves the highest residue (similar to that of ZnO) not only because it is a flame retardant that requires to absorb heat for its activation (as for the other flame retardants), but also for the release of non-flammable molecules, i.e. ammonia and water during the char formation (Shen, Kochesfahani, & Jouffret, 2010). Furthermore, it is noteworthy to underline that a joint effect occurring between BaS and silica promotes the char formation, although the mechanism, well documented in the literature, is not well understood (Horrocks, 2001).

3.3. Flame retardancy

The flame retardant properties of the treated fabrics have been evaluated in terms of combustion behaviour by cone calorimetry and compared with that of pure cotton. Table 4 summarises the collected data. From an overall point of view, the TTI values are not significantly affected by the presence of the deposited coatings, although a slight delay is observed for the samples containing APB, BP, APP and BaS, together with a small decrease of THR and pkHRR values (except for APP), as reported in Fig. 6A; the highest pkHRR decrease is observed for the silica coating alone (Fig. 6B).

For what concerns the evolved smokes (Table 4 and Fig. 7A), the average TSR (which indicatively refers to the amount of generated smokes in a full-scale fire) is strongly affected by the coating, as well as the SF is (a useful parameter able to compensate the incomplete combustion of the sol–gel treated samples, according to Horrocks et al., 2010). Indeed, the deposited coatings, protecting the fabric, favour the char formation and hinder the evolution of volatile species that fuel further degradation: as a consequence, the smoke production is significantly lowered. The cotton treated with silica coating alone has lower TSR, SF and RSR peak values with respect to the untreated fabric (11, 1.2 and 1.4 vs. 24 m^2/m^2, 2.6 MW/m^2 and 1.8 s^{-1} for CO_Si and CO, respectively). The only joint effect of silica and smoke suppressants or flame retardants has been observed

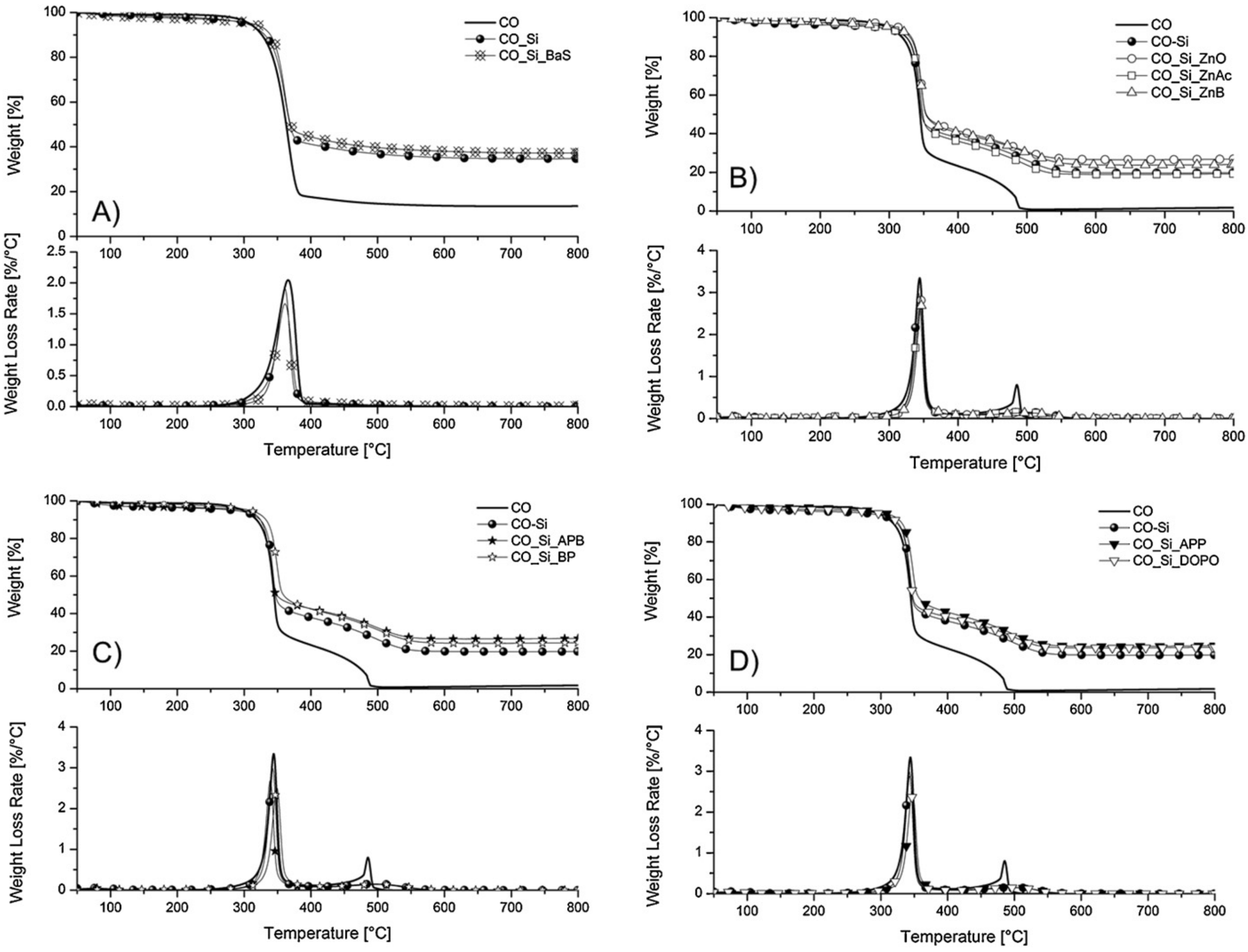

Fig. 5. TG and dTG curves of untreated and sol–gel treated cotton fabrics in air.

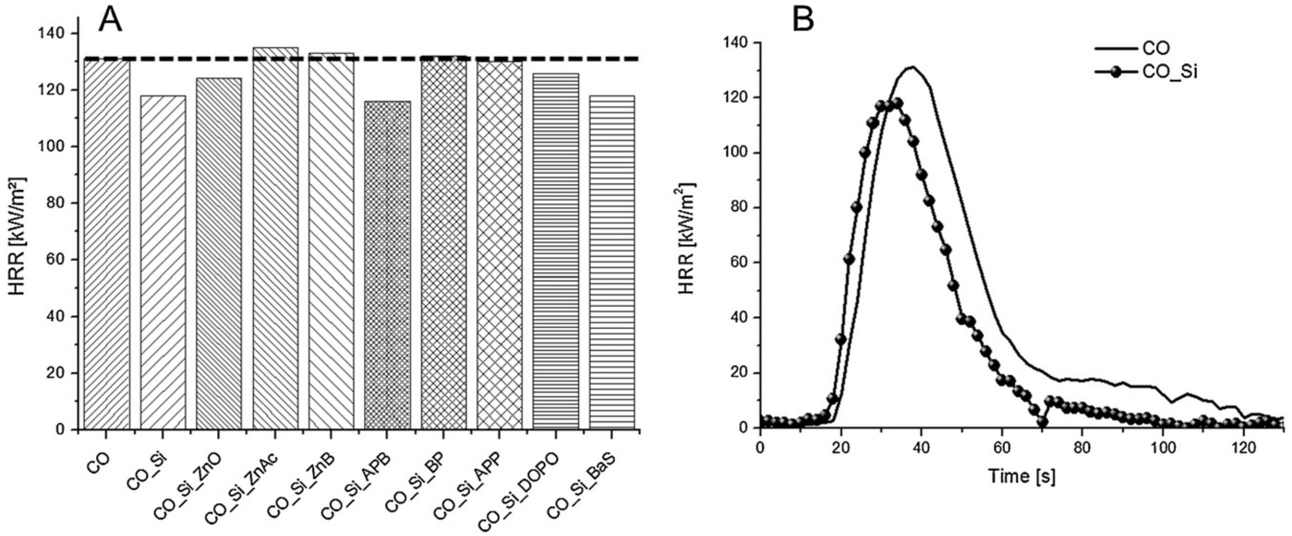

Fig. 6. HRR values of untreated and sol–gel treated cotton fabrics (A) and HRR curve of cotton and cotton treated with silica alone (B).

Table 4
Combustion data by cone calorimetry.

Sample	TTI	THR	HRR	TSR	SF[a]	RSR	CO				CO_2		Residue
	[s]	[MJ/m^2]	Peak [kW/m^2]	[m^2/m^2]	[MW/m^2]	Peak [1/s]	1° peak [ppm]	Time [s]	2° peak [%]	Time [s]	Peak [%]	Time [s]	[%]
CO	18	3.8	131	24	2.6	1.8	0.0011	36	0.0018	82	0.146	52	<1
CO_Si	18	3.3	118	11	1.2	1.4	0.0005	28	0.0045	76	0.112	48	20
CO_Si_ZnO	18	3.6	124	9	1.0	1.3	0.0002	32	0.0032	78	0.095	56	30
CO_Si_ZnAc	18	3.6	135	18	2.2	2.0	0.0004	30	0.0040	76	0.110	50	25
CO_Si_ZnB	18	3.6	133	17	2.0	1.7	0.0004	32	0.0040	76	0.108	50	29
CO_Si_APB	22	3.4	116	21	2.4	2.2	0.0008	34	0.0045	76	0.108	48	24
CO_Si_BP	20	3.6	132	25	2.9	2.8	0.0014	32	0.0048	78	0.092	52	26
CO_Si_APP	20	3.6	130	19	2.3	1.8	0.0007	32	0.0037	72	0.090	52	30
CO_Si_DOPO	18	3.6	126	14	1.7	2.0	0.0007	30	0.0038	74	0.116	46	23
CO_Si_BaS	22	3.3	118	15	1.7	1.9	0.0008	34	0.0040	82	0.100	60	25

[a] Corresponding to the HRR peak.

employing ZnO. Indeed, CO_Si_ZnO sample shows the lowest TSR, SF and RSR peak values (9 m^2/m^2, 1.0 MW/m^2 and 1.3 s^{-1}); On the other hand, the worst performances have been observed for CO_Si_BP (25 m^2/m^2, 2.9 MW/m^2 and 2.8 s^{-1}). Coherently, at the beginning of the combustion, CO_Si yields a lower amount of CO as compared to untreated cotton since the coating hinders the volatile production and favours the char formation, as reported in Fig. 7B. Subsequently, for CO_Si, the released CO increases, since the great char amount formed is continuously oxidized to CO. However, the CO_2 yield by CO_Si sample is lower than that released by pure cotton.

In the presence of zinc-based smoke suppressants, the released CO and CO_2 proved to be reduced if compared with CO_Si. The joint effect of ZnO and silica give the most significant decrease of CO and CO_2 yields. On the contrary, the combination of silica with phosphorus- or boron-based flame retardants has not shown any remarkable decrease of the CO and CO_2 production.

As clearly reported by Horrocks and co-workers, the evaluation of CO and CO_2 species in conjunction with smoke is very important for two reasons: first of all, CO and CO_2 are the main constituents of fire gases and high CO concentrations can be lethal; second, the analysis of these species can provide useful information on the mechanism of decomposition of a polymer such as cotton (Horrocks et al., 2010).

Finally, the protective role of the sol–gel treatments has been further confirmed by cone calorimetry: indeed, the residues after the test appear thick, compact and dense (Fig. 8); in addition, the highest residues are achieved in the presence of APP and ZnO (Table 4), this latter being the best smoke suppressant system among those under investigation.

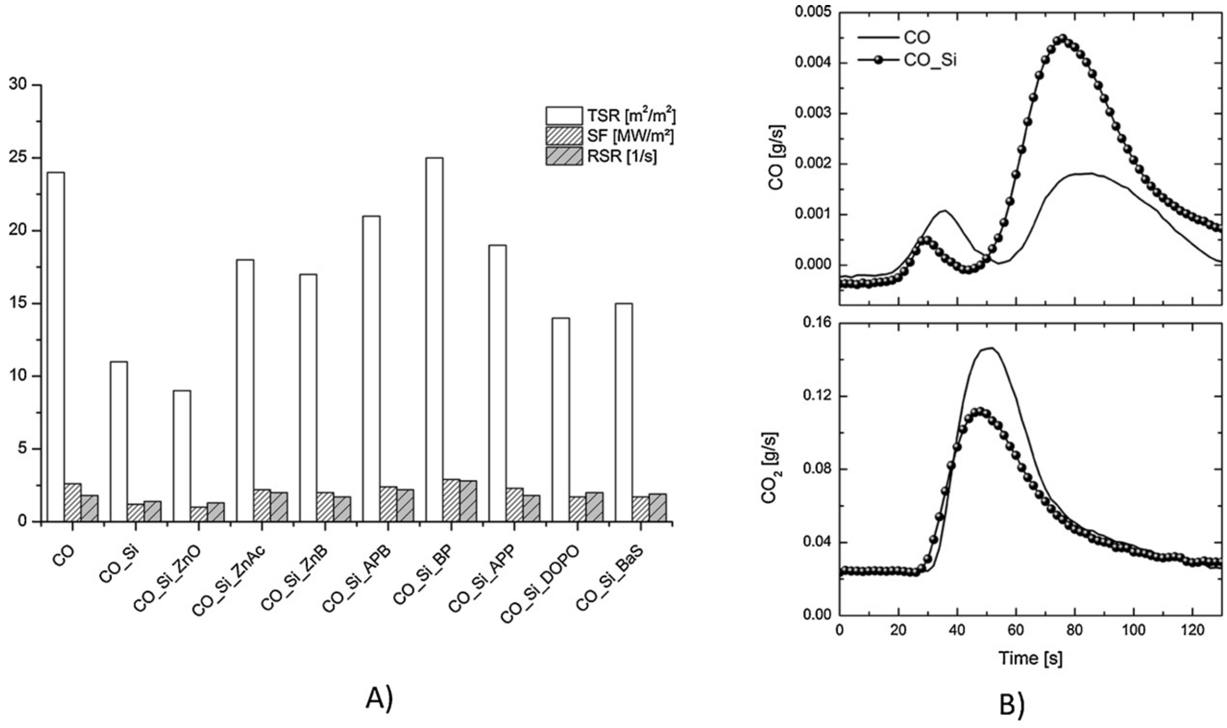

Fig. 7. TSR, SF and RSR THR values (A) and CO and CO_2 curves (B) of untreated and sol–gel treated cotton fabrics.

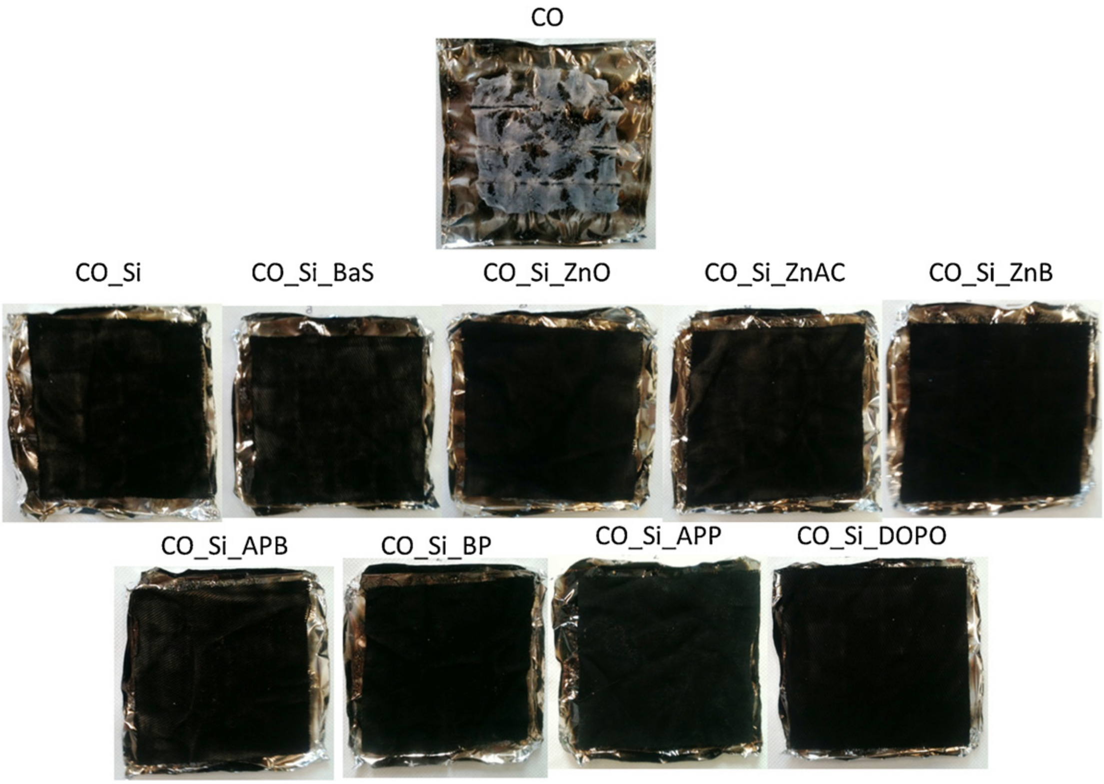

Fig. 8. Residues of untreated and sol–gel treated cotton fabrics at the end of the cone calorimetry test.

4. Conclusions

Cotton fabrics have been subjected to sol–gel treatments in the presence of different smoke suppressants (namely, zinc oxide, zinc acetate dihydrate and zinc borate) or flame retardants (i.e. ammonium pentaborate octahydrate, boron phosphate, ammonium polyphosphate and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide), or in the presence of barium sulphate, which possesses both the peculiarities. TG analyses performed in nitrogen and air have shown strong joint effects occurring between the silica phase and the smoke suppressants, which determined a significant increase of the residues at the different temperatures investigated. The morphology of the silica coating containing the smoke suppressants has been assessed by SEM and revealed that all the treated fibres have been homogeneously covered by a continuous thin film: the only exception was represented by the coatings added with zinc borate or barium sulphate, which formed microaggregates dispersed within the silica film. As assessed by cone calorimetry, in the presence of zinc-based smoke suppressants, the release of CO and CO_2 has been significantly reduced with respect to the fabric treated with the silica coating alone. In particular, the joint effect of ZnO and silica have given the most significant decrease of CO and CO_2 yields, while the combination of silica with phosphorus- or boron-based flame retardants did not achieve remarkable decreases of the CO and CO_2 production.

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