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Novel flame retardant finishing systems for cotton fabrics based on phosphorus-containing compounds and silica derived from sol–gel processes

Jenny Alongi*, Mihaela Ciobanu, Giulio Malucelli

Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, sede di Alessandria, V. Teresa Michel 5, 15121 Alessandria, Italy

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ABSTRACT

Cotton fabrics have been subjected to sol–gel processes performed in the presence of phosphorus-based compounds, in order to prepare a novel flame retardant finishing system. The effect of the concurrent presence of phosphorus and silica on the flame retardancy and combustion behaviour of cotton has been assessed through flammability tests and cone calorimetry, respectively. Furthermore, the improved thermo-oxidative stability of the treated fabrics has been evaluated by thermogravimetric analysis in air. The obtained results have shown the efficiency of the novel flame retardant finishing system and its durability, as well.

1. Introduction

During the last two decades, the need of durable flame retardant finishing systems for cotton has become an urgent exigency that has addressed both the academic and industrial research activities to explore novel synthetic strategies based on the known chemistry. Notable efforts and interests have been focused on the enhancement of the char-forming efficiency by using intumescent systems, able to create a physical barrier onto the textile surface, thus protecting the polymer bulk (Horrocks, 1996, 2010). This approach has been employed for different polymer matrices such as polyamide 6, poly(ethylene terephthalate) and polypropylene, with promising and encouraging results. The efficiency of these systems was found to increase when added of nanoparticles synthesized by different approaches (Bourbigot, Devaux, & Flambard, 2002; Chen et al., 2005; Zhang, Horrocks, Hull, & Kandola, 2006).

To this aim, the sol–gel technique represents a versatile synthetic route based on two steps of hydrolysis and condensation reactions, starting from (semi)metal alcoxides (tetraethoxysilane, tetramethoxysilane, titanium tetraisopropoxide, etc.) that leads to the formation of organic–inorganic hybrid coatings at or near room temperature (Sakka, 2003). These coatings are capable to protect the polymer surface by creating a physical barrier acting as insulators. In previous works, our research group has already demonstrated that it is possible to exploit this approach for enhancing the flame retardancy of cotton (Alongi, Ciobanu, Carosio, Tata, & Malucelli, 2011; Alongi, Ciobanu, & Malucelli, 2011).

Usually, classical flame retardant treatments for cellulosic materials exploit the use of phosphorus/nitrogen-based compounds, as widely discussed in the literature (Cole, 1979; Cole & Stephenson, 1980; Hebeish, Waly, and Abou-Okeil, 1999; Yang, Wu, and Xu, 2005). Flame retardancy properties are evaluated through flammability tests, such as Limiting Oxygen Index (Beninate, Trask, & Drake, 1981; Cheng & Yang, 2009; Cullis, Hirschler, & Madden, 1992; Tian et al., 1999; Wu & Yang, 2006, 2007; Yang & Wu, 2003a, 2003b), vertical flame tests (based on ASTM D1230) (Liodakis, Fetsis, & Agioviasitis, 2009; Mostashari & Baie, 2008; Mostashari & Baie, 2009; Mostashari & Fayyaz, 2008) or others standards (Wu & Yang, 2008). Such tests have also been performed on cotton blends (Li et al., 2010; Yang & Yang, 2005); in any case, they can provide only partial information concerning the burning behaviour of a polymeric material. Indeed, flame retardancy is a term that can express either the material's ignitability or its combustion behaviour. In the first case, it is possible to measure how a material reacts when a flame is applied for a certain time: such parameters as ignitability, dripping, total burning time and final residue are evaluated. On the other side, the combustion behaviour allows to investigate how a material burns when it is irradiated by a heat flow developed by the flame spread: time to ignition, total heat release and corresponding rate, total smoke release and corresponding optical density are measured. Usually, this latter test can be carried out using sophisticate instrumentations based on calorimetry, such as radiating panel (ISO 9323 standard) or cone calorimeter (ISO 5660 standard).

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

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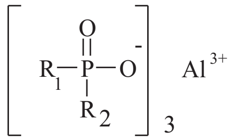
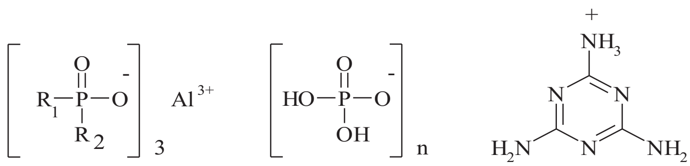
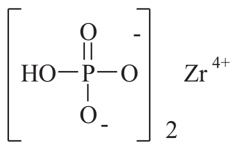
Table 1
Chemical formula of the phosphorus-based flame retardants used.

Code	Chemical formula	Name
AP Exolit®OP1230		Aluminium phosphinate
APMP Exolit®OP1312	 $2ZnO\ 3B_2O_3$	Aluminium phosphinate (63.5%)[a] + melamine polyphosphate (32%)[a] + zinc and boron oxide (4.5%)[a]
ZrP		α-Zirconium dihydrogen phosphate

[a] wt.%.

Flammability and combustion tests provide any helpful and complementary information in order to thoroughly describe a realistic fire scenario. For this reason, in the present paper, both these tests have been employed for measuring the flame retardant properties of cotton fabrics, sol–gel treated in the presence of phosphorus-containing compounds. The aim of this work is to assess and demonstrate the improvements in the flame retardant properties of cotton, due to the concurrent presence of phosphorus and silica. To our best knowledge, only few scientific papers on this topic have been published in the literature so far. Although not directly referring to cotton, Yaman investigated the effect of sol–gel phosphate-based flame retardant coating on flammability, stiffness, and strength of polyacrylonitrile fabrics (Yaman, 2009). Cireli et al. have synthesized phosphorus-doped silica thin films by using sol–gel processes in the presence of phosphoric acid or ethyldichloro phosphate, to be used as novel flame retardant finishing systems for cotton. These films have shown enhanced flame retardancy properties (Cireli et al., 2007). Similarly, Brancatelli et al. have very recently exploited the synergistic effect of silica (derived from sol–gel processes) and phosphorus to enhance the thermal stability and flame retardancy of cotton fabrics (Brancatelli, Colleoni, Massafra, & Rosace, 2011).

The thermo-oxidative behaviour of the so treated fabrics has been also investigated by means of thermogravimetric analysis in air.

Finally, the durability of the sol–gel treatment has been assessed, as well.

2. Experimental part

2.1. Materials

Cotton fabric (purchased from Zhejiang Zhongda Textiles Co. Ltd., China) with a density of 210 g/m^2 (the number of threads per unit length is 33 and 11 for weft and warp, respectively) was used as received. Tetramethoxysilane (TMOS), water, ethanol and dibutyltindiacetate (all reagent grade) were purchased from Sigma–Aldrich and used as received. Two commercial phosphorus-based flame retardants (containing ca. 20 wt.% of phosphorus) were supplied by Clariant Inc. (France). Their tradenames are Exolit®OP1230 and Exolit®OP1312; their structure is schematized in Table 1. As far as Exolit®OP1312 is concerned, it consists of aluminium phosphinate (63.5 wt.%), melamine polyphosphate (32 wt.%), zinc and boron oxide (4.5 wt.%).

Furthermore, an α-zirconium dihydrogen phosphate (coded as ZrP, Table 1) was purchased from Prolabin & Tefarm s.r.l. (Italy).

2.2. Preparation of sol–gel treated cotton fabrics

Pure silica phases were synthesized by the sol–gel technique using TMOS (as silica precursor), water, ethanol and dibutyltindiacetate: a mixture containing TMOS, ethanol and distilled water (TMOS:H_2O molar ratio = 1:1) was stirred at room temperature for 10 min; dibutyltindiacetate (0.9 wt.%) was added as condensation catalyst. Then, the cotton fabrics were impregnated at room temperature in the sol solution (1 min) and, subsequently, thermally treated at 80 °C for 15 h using a gravity convection oven. Hereinafter, these samples will be coded as TMOS.

In order to avoid a possible drastic loss of mechanical properties of the cotton substrate, as already assessed in a previous work (Alongi, Ciobanu, & Malucelli, 2011), the sol solution was prepared at neutral pH.

With the aim of investigating the effect of the combination of silica prepared by sol–gel with phosphorus compounds, three commercial flame retardants (Table 1) were added to the sol solution containing the silica precursor and then cotton fabrics were impregnated following the above described procedure. All the prepared formulations are collected in Table 2.

For a preliminary study, aluminium phosphinate (AP, Table 1) was used as model molecule for optimizing the flame retardant content; to this aim, different amounts of AP (namely, 5, 15, 30 and 50 wt.% with respect to TMOS content) were employed.

All AP formulations were prepared by adding the additive in the sol solution during the silica preparation: the only exception is TMOS 5AP* for which initially the cotton fabric was sol–gel treated according to the procedure described for TMOS and subsequently dipped in a weakly alcoholic AP solution (5 wt.%) for 1 h, squeezed and dried in a gravity convection oven at 80 °C.

Furthermore, samples containing 15 wt.% of APMP and of ZrP were prepared, as well.

Table 2
Formulations investigated for cotton fabrics.

Code	[TMOS][a]	Phosphorus flame retardant content [wt.%]	A^d [wt.%]
TMOS	Yes	0	19
TMOS 5AP	Yes	5	19
TMOS 5AP*[b]	Yes	5	22
TMOS 15AP	Yes	15	21
TMOS 30AP	Yes	30	22
TMOS 50AP	Yes	50	23
TMOS 15APMP	Yes	15	22
TMOS 15ZrP	Yes	15	22
5AP	No	5	2
15AP	No	15	4
15APMP	No	15	4
15ZrP	No	15	5
TMOSw[c]	Yes	0	20
5APw[c]	No	5	2
TMOS 5APw[c]	Yes	5	21
TMOS 5AP*w[c]	Yes	5	23
TMOS 15APw[c]	Yes	15	23
TMOS 15APMPw[c]	Yes	15	24
TMOS 15ZrPw[c]	Yes	15	24

[a] TMOS:H_2O molar ratio = 1:1.
[b] Sample initially treated by sol–gel method and subsequently dipped into an alcoholic phosphorus compound solution.
[c] Samples washed for 1 h at 60 °C in distilled water.
[d] Weight difference of cotton fabrics before and after impregnation/thermal treatment.

2.3. Characterization techniques

In order to describe a realistic fire scenario, it is important to test both the ignitability of a sample in the presence of a flame spread (flammability) and the combustion behaviour of the same sample under the irradiative heat flow, developed as a consequence of the flame exposure. Therefore, the flame retardancy properties of the prepared samples were measured through two different tests.

The flammability test in vertical configuration was carried out by applying a methane flame for 5 s at the bottom of a fabric specimen (50 mm × 150 mm) and repeating the application at least two times. Alternatively, when the test was performed in horizontal configuration, the flame was applied on the short side of the specimen (50 mm). These tests were repeated five times for each formulation. Total burning time and kinetics after the flame applications (burning rate at 30 and 60 mm of the specimen) and the final residue were measured. A Flammability Performance Index (FlaPI, %/s) was also calculated as the ratio of final residue to total burning time: the higher the FlaPI, the better is the flame retardancy performance.

Furthermore, cone calorimetry (Fire Testing Technology, FTT) was employed to investigate the combustion behaviour of 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 correct 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 peak (pkHRR, kW/m^2), effective heat of combustion (EHC, MJ/kg) and mass loss rate (MLR, g/s) were measured. The Fire Performance Index (FPI, s m^2/kW) was also calculated as TTI to pkHRR ratio. The higher the FPI, the better is the flame retardancy performance (Schartel, Bartholmai, & Knoll, 2006). Total smoke release (TSR, m^2/m^2), specific extinction area (SEA, m^2/kg), CO and CO_2 yield ([CO] and [CO_2], kg/kg) were evaluated, as well.

For each sample, the experiments were repeated four times in order to ensure reproducible and significant data. The experimental error was within 2%.

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. A Pyris1TGAQ500 analyzer was used, placing the samples in open alumina pans, in air atmosphere (60 ml/min).

The surface morphology of the treated samples was studied using a Field-Emission Scanning Electron Microscope (FESEM, ZEISS SUPRA55VP). In addition, a scanning electron microscope (SEM, LEO-1450VP), equipped with a X-ray probe (INCA Energy Oxford, Cu Kα X-ray source, k = 1.540562 Å), was used to perform elemental analysis. Fabric pieces (0.5 mm × 0.5 mm) were cut and fixed to conductive adhesive tapes and gold-metallized.

The amount of material charged on the cotton samples (A, wt.%) was determined by weighting each sample before (W_i) and after the impregnation in the sol solution and the subsequent thermal treatment (W_f), using a Sartorius balance (±10^{-4} g). The upload, collected in Table 2, was calculated according to the following formula:

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

Finally, the durability of some treated fabrics was evaluated by performing a washing treatment for 1 h at 60 °C with distilled water.

3. Results and discussion

3.1. Combustion behaviour

As already shown in previous works (Alongi, Ciobanu, Carosio, et al., 2011; Alongi, Ciobanu, & Malucelli, 2011), the sol–gel method is an efficient flame retardant finishing system for cotton. Indeed, comparing the neat fabric with the treated sample (TMOS) (Table 3), it is clear that the presence of the silica coating onto the textile surface modifies the combustion behaviour of cotton by decreasing the total heat release (2.5 MJ/m^2 *vs.* 2.8 MJ/m^2 for neat cotton), the mass loss rate (0.021 g/s *vs.* 0.029 g/s) and, consequently, the effective heat of combustion (14.1 MJ/kg *vs.* 15.2 MJ/kg). This finding points out that the silica coating is able to protect the polymer from oxygen and heat transfer, blocking its decomposition. Indeed, the amount of polymer available to burn is lower as compared with neat cotton, as shown by EHC and MLR decrease. Since THR decreases, the heat release rate peak decreases as well (namely, 81 kW/m^2 *vs.* 91 kW/m^2 for TMOS and cotton, respectively). The silica coating is also responsible for TTI increase, since it is able to delay the ignition of the sample (28 s *vs.* 14 s). These results are in agreement with those reported in the literature (Lecoueur, Vroman, Bourbigot, Lam, & Delobel, 2001). Regarding the Fire Performance Index, TMOS is characterized by enhanced flame retardant properties in comparison with neat cotton, as evidenced by the highest FPI value (0.34 s m^2/kW *vs.* 0.15 s m^2/kW). Smoke release represents a further important feature to highlight during the combustion process: the total smoke release (TSR), the amount of evolved carbon monoxide and dioxide ([CO] and [CO_2] yields), as well as the optical density of released smokes (expressed as specific extinction area), decrease in a remarkable way (Table 3).

Pursuing this research, a commercial flame retardant as aluminium phosphinate (AP) has been combined with the sol–gel treatment in order to verify the effect of the concurrent presence of phosphorus, which acts in condensed phases, with ceramizing silica domains, on the flame retardant properties of the treated cotton fabrics. Indeed, in the literature, the capabilities of phosphorus compounds as flame retardants for cotton are well known (Horrocks, 2000, chap. 4). To this aim, different amounts of AP (namely, 5, 15, 30 and 50 wt.% with respect to TMOS content) have been considered: with the only exception of TMOS 5AP*, all AP-based formulations were prepared by adding the additive to the

Table 3
Collected data of phosphorus-based formulation by cone calorimetry.

Sample	TTI [s]	pkHRR [kW/m^2]	FPI [s m^2/kW]	THR [MJ/m^2]	MLR [g/s]	EHC [MJ/kg]	TSR [m^2/m^2]	SEA [m^2/kg]	[CO] yield [kg/kg]	[CO_2] yield [kg/kg]
Cotton	14	91	0.15	2.8	0.029	15.2	21.4	25.4	0.0333	2.39
TMOS	28	81	0.34	2.5	0.021	14.1	18.3	21.2	0.0250	2.19
TMOS 5AP	26	79	0.33	2.6	0.022	14.4	24.2	32.4	0.0491	2.31
TMOS 5AP*	17	118	0.14	3.2	0.030	15.0	27.6	45.6	0.0470	2.26
TMOS 15AP	29	89	0.32	2.6	0.023	13.8	42.6	67.3	0.0512	2.32
TMOS 30AP	29	105	0.28	3.0	0.029	18.2	77.1	344.3	0.0690	2.55
TMOS 50AP	44	120	0.37	4.1	0.030	24.9	155.6	372.6	0.0921	2.77
TMOS 15APMP	23	100	0.23	2.5	0.020	16.6	79.0	220.4	0.0820	3.03
TMOS 15ZrP	22	107	0.21	2.9	0.020	19.8	84.6	259.5	0.0805	3.67
5AP	19	90	0.21	2.7	0.028	15.1	26.2	30.7	0.0483	2.39
15AP	28	95	0.29	2.6	0.027	15.0	41.7	56.2	0.0722	2.68
15APMP	38	80	0.48	1.9	0.022	10.7	72.8	35.0	0.1067	2.23
15ZrP	35	93	0.38	2.6	0.022	18.4	20.2	32.2	0.0501	2.11
TMOSw	46	80	0.58	2.2	0.020	15.3	67.4	48.7	0.0494	2.62
5APw	27	124	0.21	2.6	0.022	14.5	37.4	84.8	0.0554	2.78
TMOS 5APw	40	101	0.40	2.8	0.020	13.4	31.3	21.2	0.0286	2.26
TMOS 5AP*w	32	92	0.35	2.5	0.021	15.2	42.9	23.4	0.0422	2.50

sol solution during the preparation of silica. TMOS 5AP* was prepared as a reference in order to compare the mixing procedure of the phosphorus compound with silica.

Comparing cotton and TMOS with the phosphinate/sol–gel treated counterparts (Table 3, Fig. 1), it is worthy to note that by increasing the AP content, THR, MLR and, consequently, EHC and pkHRR substantially increase. In spite of this trend, the FPI turns out to be higher than cotton and comparable with TMOS because the TTI increases in remarkable way, up to 44 s for TMOS 50AP. The worsening of FPI is mainly attributable to the presence of phosphorus compounds; indeed, it is possible to observe lower FPIs and higher heat and smoke release for 5AP and 15AP in comparison with the corresponding phosphinate/sol–gel treated counterparts (TMOS 5AP and TMOS 15AP, respectively). The scarce solubility of AP within the weakly alcoholic solution could not allow to treat cotton fabrics with high amounts of aluminium phosphinate (*i.e.* 30AP and 50AP samples): therefore, we limited our investigation to 15AP (Table 3).

Comparing TMOS 5AP with TMOS 5AP*, it is possible to notice that the best method for combining the phosphorus compound with silica is to add AP directly to the sol solution because the formed silica coating protects AP limiting the anticipation of cotton ignition.

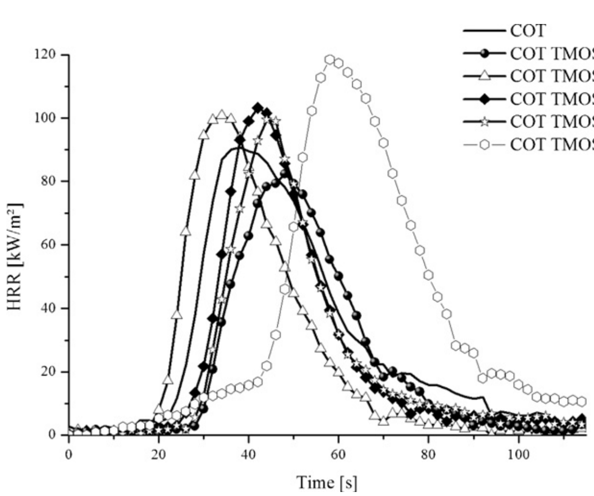


Fig. 1. HRR curves of COT TMOS AP formulations.

On the basis of these results, TMOS 5AP and TMOS 15AP seem to be the most promising formulations, although their TSR and SEA values turn out to be higher than those of TMOS.

Since a synergistic effect between nitrogen and phosphorus compounds, as already described in the literature (Alongi & Frache, 2010; Cheng & Yang, 2009; Wu & Yang, 2007) may help to further improve the final fire retardancy and combustion behaviour of cotton fabrics, we chose to compare APMP with AP (*i.e.* TMOS 15APMP *vs.* TMOS 15AP), using 15 wt.% as APMP optimal additive content, as suggested by its supplier. In addition, we also considered a multilamellar nanometric α-zirconium dihydrogen phosphate (ZrP), the flame retardant properties of which have already been described in the literature (Alongi & Frache, 2010). In the presence of both these additives, the fire performances are not enhanced with the exception of the kinetics of the burning process (mass loss rate, MLR, slowly decreases). This trend has also been confirmed in the vertical flame tests, as depicted by FlaPI values collected in Table 4.

Comparing the final residues obtained by cone calorimeter (Fig. 2), it is possible to observe that the phosphorus-based flame retardants alone are not able to maintain the initial texture of cotton, unlike the silica coating, alone or coupled with them. As previously demonstrated, the silica coating takes advantage of the presence of phosphorus, favouring the ceramization of cotton under the irradiative heat flow.

Although its performances are comparable with those of TMOS, TMOS 5AP was chosen as a reference for testing the durability of the treatment, which may represent a key factor when a possible industrial exploitation is foreseen. Table 3 shows that the fire performances of TMOS are improved by washing the sample for 1 h at 60 °C because the sol–gel process further occurs, as already reported in the literature (Alongi, Ciobanu, & Malucelli, 2011). In spite of a higher FPI with respect to cotton, the smoke release and optical density of TMOSw increase (Table 3). On the other hand, the fabric treated with AP alone worsens its flame retardancy properties, since aluminium phosphinate is leached out the treated fabric during washing. Therefore, we can conclude that the combination of the flame retardant with the silica coating allows to strongly enhance the overall fire performances even after washing the treated fabric with distilled water.

3.2. Flammability test

The results of flammability test in vertical and horizontal configuration are collected in Tables 4 and 5, respectively. First of all,

Table 4
Collected data of phosphorus-based formulation by flammability test in vertical configuration.

Sample	Number of flame applications[a]	Total burning time [s]	Time at 30 mm [s]	Rate at 30 mm [mm/s]	Time at 60 mm [s]	Rate at 60 mm [mm/s]	Residue [%]	FlaPI [%/s]
Cotton	1	38	4	7.50	9	6.66	14	0.37
TMOS	2	41	10	3.00	13	4.62	34	0.85
5AP	1	34	7	4.28	11	5.45	17	0.50
15AP	3	35	5	16.66	7	8.57	31	0.88
15APMP	2	45	7	4.29	9	6.66	45	1.00
15ZrP	3	43	4	7.50	6	10.00	18	0.42
TMOS 5AP	2	38	9	3.33	13	4.62	40	1.05
TMOS 5AP[a]	2	37	7	4.29	12	5.00	41	1.10
TMOS 15AP	3	35	10	3.00	12	5.00	55	1.57
TMOS 15APMP	2	38	10	3.00	14	4.29	50	1.32
TMOS 15ZrP	4	110	11	2.73	29	2.07	62	0.56
TMOSw	1	43	7	4.28	10	6.00	51	1.19
5APw	1	27	4	7.50	7	8.57	14	0.52
TMOS 5APw	1	28	6	5.00	9	6.66	36	1.28
TMOS 5AP[a]w	1	34	7	4.29	10	6.00	38	1.12
TMOS 15APw	2	34	11	2.72	16	3.75	64	1.88
TMOS 15APMPw	1	36	12	2.50	15	4.00	48	1.33
TMOS 15ZrPw	1	33	10	3.00	13	4.61	60	1.82

[a] The flame has been applied for 5 s.

the sol–gel process is able to modify cotton flammability in vertical configuration (Table 4) by (i) decreasing its ignitability when cotton is exposed to a flame spread (indeed, 2 flame applications instead of 1 are necessary to ignite it), (ii) decreasing its kinetics of burning (at 30 and 60 mm) and (iii) increasing the total burning time. Thus, the silica coating is able to protect the cotton fabric: indeed, the final residue of TMOS is higher than neat cotton (34% *vs.* 14%). If cotton is treated with 15 wt.% of AP, APMP or ZrP, the combustion is more rapid, as observed by comparing the burning rates at 30 and 60 mm; nevertheless, the final residue is higher than that of the pristine substrate (31%, 45% and 18% *vs.* 14%). Considering the Flammability Performance Index (FlaPI), 5AP shows higher performances than neat cotton, but lower than TMOS (0.50%/s *vs.* 0.37%/s and 0.85%/s, respectively). In the case of the concurrent presence of phosphorus compounds and silica, all the obtained formulations, regardless of phosphorus type and content, have been turned out to be more efficient than cotton, TMOS or cotton treated with only phosphorus compounds. In particular, TMOS 5AP, TMOS 15AP and

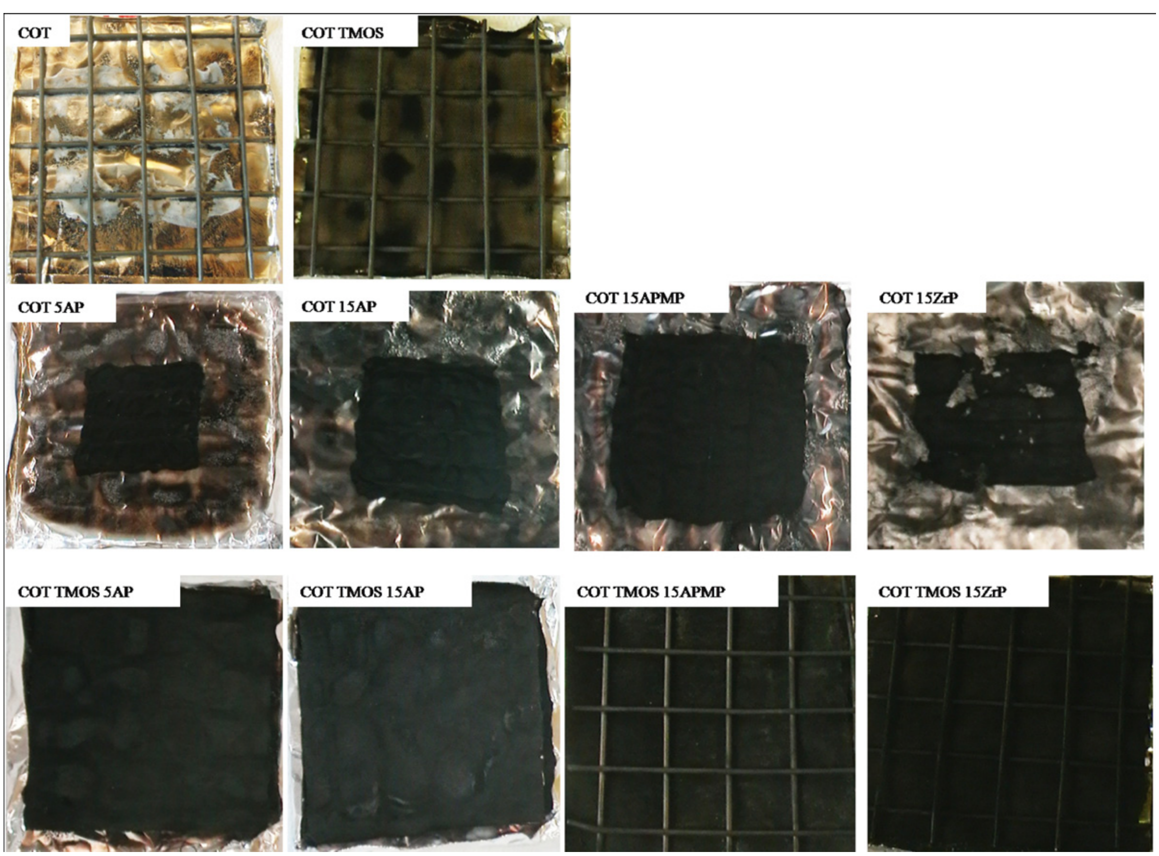


Fig. 2. Pictures of final residues of cotton fabrics after cone calorimeter tests.

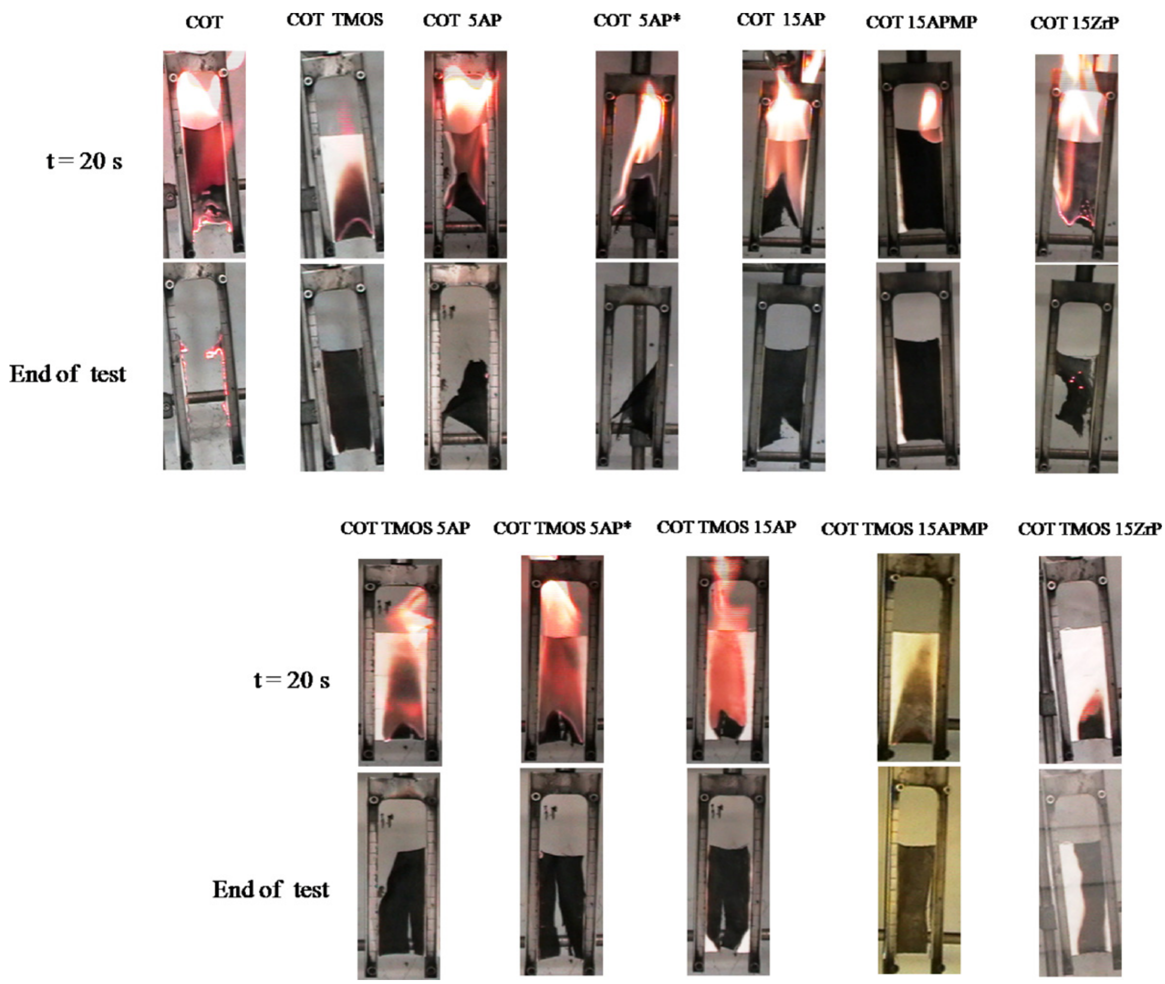


Fig. 3. Pictures of final residues of cotton fabrics after flammability test in vertical configuration.

TMOS 15APMP show an increase of FlaPI with respect to neat cotton. On the contrary, although TMOS 15ZrP shows a low FlaPI, its burning rate is very slow (110 s of total burning time) and it is possible to ignite the sample only after 4 flame applications. In addition, TMOS 15ZrP evidences the highest final residue (62%) among all the investigated formulations.

In any case, the flammability test demonstrates that a synergistic effect between phosphorus-based compounds and silica occurs and is still maintained when the samples are subjected to the washing treatment with distilled water at 60 °C. As a matter of fact, FlaPI of TMOS 5APw and TMOS 5APw* is higher than that of neat cotton, TMOS and 5APw. A similar trend

Table 5
Collected data of phosphorus-based formulation by flammability test in horizontal configuration.

Sample	Number of flame applications[a]	Total burning time [s]	Time at 30 mm [s]	Rate at 30 mm [mm/s]	Time at 60 mm [s]	Rate at 60 mm [mm/s]	Residue [%]	FlaPI [%/s]
Cotton	1	150	23	1.30	95	0.63	11	0.07
TMOS	1	117	43	0.70	87	0.70	59	0.50
5AP	1	103	37	0.81	77	0.78	29	0.28
15AP	1	38	28	1.07	No flame	–	36	0.53
15APMP	1	20	No flame	–	–	–	49	2.45
15 ZrP	1	158	16	1.87	52	1.15	17	0.11
TMOS 5AP	1	34	No flame	–	–	–	90	2.65
TMOS 5AP[a]	1	118	30	1.00	No flame	–	76	0.64
TMOS 15AP	2	2	No flame	–	–	–	92	46.0
TMOS 15APMP	2	2	No flame	–	–	–	98	49.0
TMOS 15ZrP	2	111	28	1.07	79	0.76	>99	>49.5
TMOSw	1	113	38	0.79	82	0.73	48	0.42
5APw	1	70	27	1.11	52	1.15	25	0.36
TMOS 5APw	1	90	17	1.76	67	0.90	78	0.87
TMOS 5AP[a]w	1	112	30	1.00	80	0.75	72	0.64

[a] The flame has been applied for 5 s.

Table 6
Thermogravimetric data of phosphorus-based formulations in air.

Sample	T_{max_1} [a] [°C]	T_{max_2} [a] [°C]	Residue at 360 °C [%]	Residue at 500 °C [%]	Residue at 750 °C [%]	Residue at 1100 °C in oven [%]
Cotton	347	472	22	4	3	<1
TMOS	349	487	37	25	24	21
5AP	328	486	30	4	4	<2
15AP	332	490	29	2	2	<2
15APMP	324	488	35	12	3	3
15ZrP	335	477	26	14	5	5
TMOS 5AP	331	487	44	29	26	21
TMOS 5AP[a]	320	488	38	28	14	15
TMOS 15AP	345	415	49	34	28	26
TMOS 15APMP	340	537	54	41	32	28
TMOS 15ZrP	344	498	48	34	31	28

[a] From derivative TG curves.

was observed in the presence of higher amounts of phosphorus.

The pictures of the sol–gel treated specimens containing phosphorus, after the ignition (at 20 s) and at the end of the burning test, evidence that the fabric texture is unchanged (Fig. 3). By examining these samples during the burning process, it can be supposed that, initially, the phosphorous compound acts as a flame retardant by limiting the degradation of cellulose and, then, the silica coating stops the further combustion of the polymer by creating a ceramic barrier onto the textile surface.

The burning tests performed in horizontal configuration (Table 5) evidence a different behaviour: indeed, the cotton texture employed in the present study is not isotropic because the weft is more dense than the warp (33 *vs.* 11 as number of threads per unit length) and, since in this configuration the specimen has been burned along the weft direction, the observed burning kinetics turns out to be slower than that measured in vertical configuration, where burning occurs along the warp direction. In general, the kinetics in horizontal configuration is slower and the total burning time is higher with respect to vertical configuration tests, with the exception of 15AP, 15APMP and the corresponding sol–gel treated samples. Such samples burn very rapidly, but they stop to burn in a short time, thus assuring high flammability resistance: in particular, TMOS15 AP and TMOS 15APMP burn out after only 2 s.

We can conclude that the formulations containing phosphorus and silica seem to be very promising, as evidenced by the total burning time (only 2 s), final residue (92% and 99%, respectively) and by their high FlaPI. Also in horizontal configuration, TMOS 15ZrP burns very slowly (111 s of total burning time) leaving the highest final residue (>99%).

3.3. Thermal stability

The thermal stability of the formulations under study has been investigated by thermogravimetric analyses.

In air, the presence of phosphorus flame retardants alone is not able to improve the thermal stability of the cotton fabrics, as reported in Table 6 and according to the literature (Gaan & Sun, 2007a, 2007b). Indeed, during the thermal decomposition, phosphorus flame retardants acting in condensed phases form phosphoric acid and polyphosphoric acids that dehydrate cellulose and thus accelerate the kinetics of the thermal oxidation.

Meanwhile, TG analyses performed in air show a synergistic effect of phosphorus and silica: indeed, all the formulations exhibit an increase of the residue formation at 360, 500 and 750 °C, (Table 6) since the carbonization step of cellulose is favoured. As an example, the TG and dTG curves of TMOS 5AP and TMOS 15AP are plotted in Fig. 4. In addition, it is worthy to note that phosphorus anticipates the thermo-oxidative degradation of cotton up to 350 °C.

As reported in the literature (Gaan & Sun, 2007a, 2007b; Horrocks, Wang, Hall, Sunmonu, & Pearson, 2000), cotton decomposes through three steps: the first (300–400 °C) involves two competitive pathways, which yield aliphatic char and volatile products; in the second and third step (400–800 °C), some aliphatic char converts to aromatic, yielding CO and CO_2 as a consequence

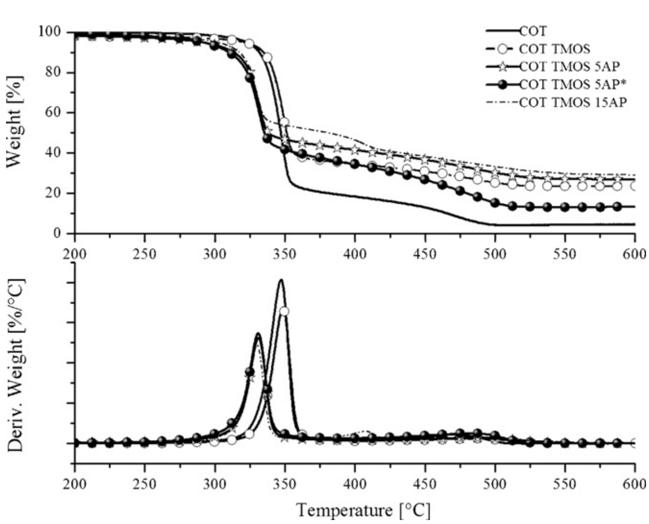


Fig. 4. TG and dTG curves of COT TMOS AP formulations.

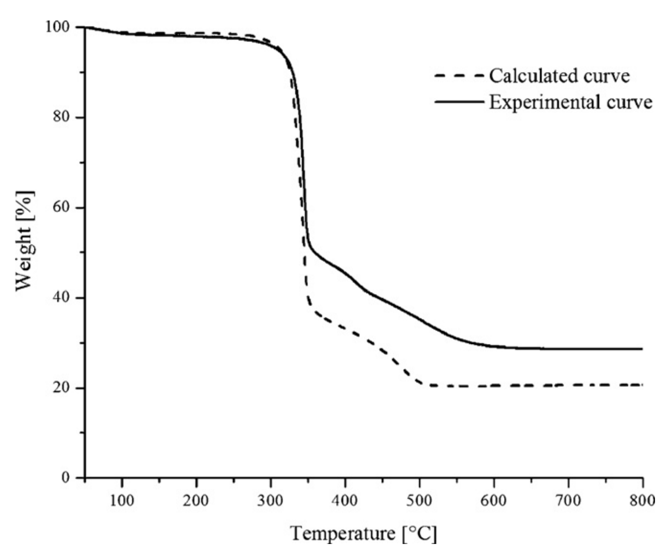


Fig. 5. Calculated and experimental TG curves of COT TMOS 15AP.

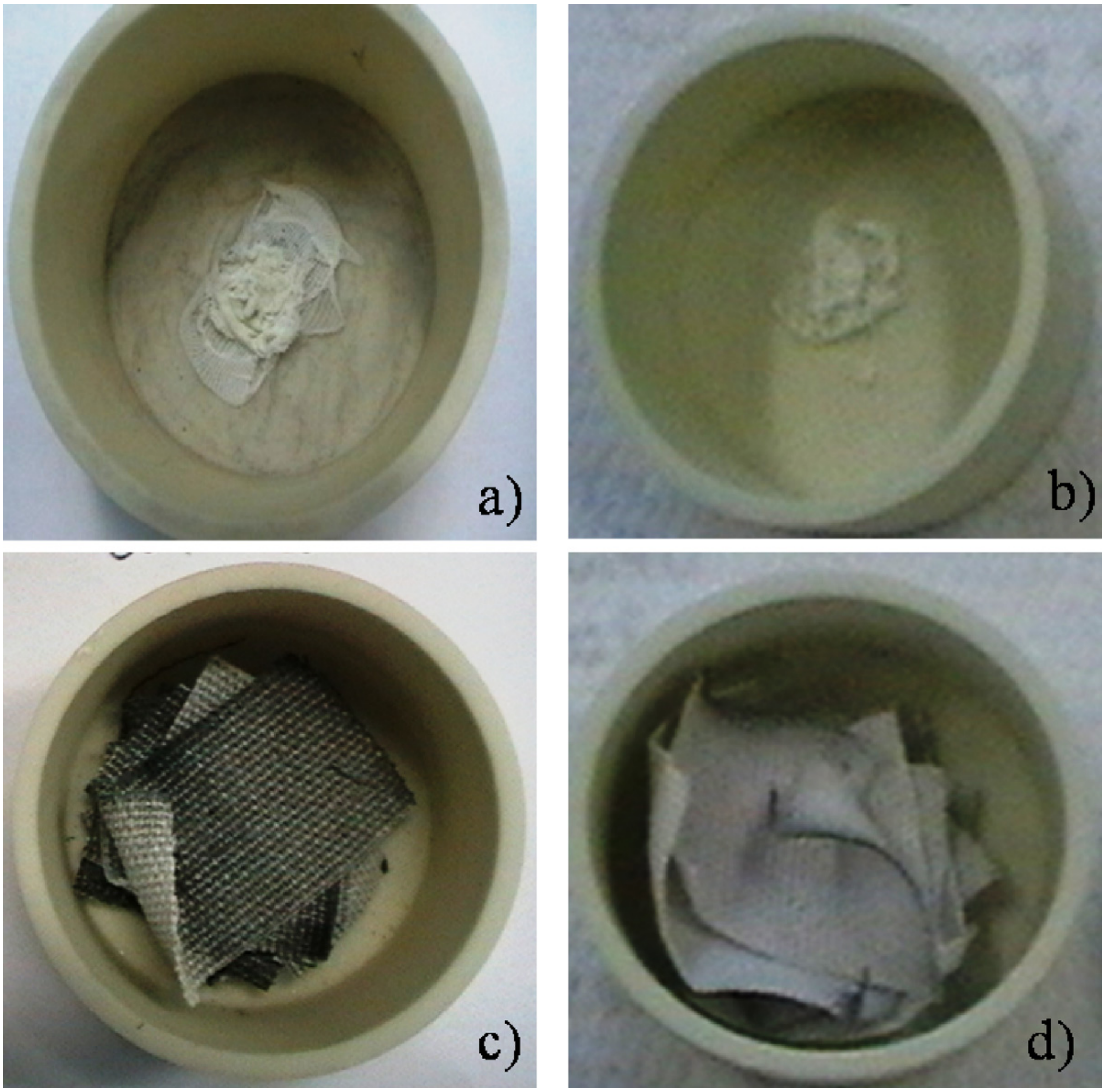


Fig. 6. Pictures of final residues of cotton fabrics after a thermal treatment at 1100 °C.

of simultaneous carbonisation and char oxidation. In the present work, two decomposition steps are observed between 300 and 550 °C. In the presence of silica alone and in couple with phosphorus, the degradation profile of cotton strongly changes: indeed, the first step is favoured and, consequently, the char formation occurs, whereas the second step almost disappears (the T_{max_2} values collected in Table 6 are negligible). Once again, this behaviour can be ascribed to the protective role of silica coating on cotton in air that favours the cellulose carbonisation at ca. 360 °C, as already demonstrated in previous works (Alongi, Ciobanu, Carosio, et al., 2011; Alongi, Ciobanu, & Malucelli, 2011). Furthermore, in the presence of phosphorus compounds, this phenomenon is more and more remarkable because the concurrent presence of the two species mainly promotes the carbonization step unlike the sol–gel treatment alone. The existence of any chemical and/or physical interaction between phosphorus and silica has been assessed by comparing the experimental with the calculated TG curves. This latter has been plotted on the basis of additivity rules, estimating the contribution of each species independently. As an example, Fig. 5 plots the calculated and experimental thermogravimetric curves of TMOS 15AP in air: it is worthy to note that the two weight losses overlap up to ca. 350 °C. Above 350 °C, the experimental curve decreases much more slowly since a thermally stable carbonaceous residue (ca. 50%) is formed. This char appears more stable than the calculated one (ca. 36%).

In addition, TMOS 15AP shows higher residues with respect to cotton and TMOS (Table 6): 49% *vs*. 22% and 37% at 360 °C, 34% *vs*. 4% and 25% at 500 °C, 28% *vs*. 3% and 24% at 750 °C, respectively. This phenomenon, that is common to all the investigated formulations, can be ascribed to a higher carbonization effect of TMOS induced by the presence of AP. This trend further confirms the synergistic effect between silica and phosphorus.

Also in this case, as previously stated by cone calorimetry, the best method for combining phosphorus compounds with silica is to add AP to the sol solution, rather than dipping the sol–gel treated fabrics in a weakly alcoholic AP solution (TMOS 5AP* *vs*. TMOS 5AP).

Finally, Table 6 (last column) and Fig. 6 show that the combination of phosphorus compounds with silica is efficient also at very high temperatures, forming a char stable up to 1100 °C. This carbonaceous structure is still able to preserve the fabric texture of TMOS and TMOS 15AP (Fig. 6c and d, respectively) in contrast with the scarce residue exhibited by cotton and 15AP (Fig. 6a and b, respectively).

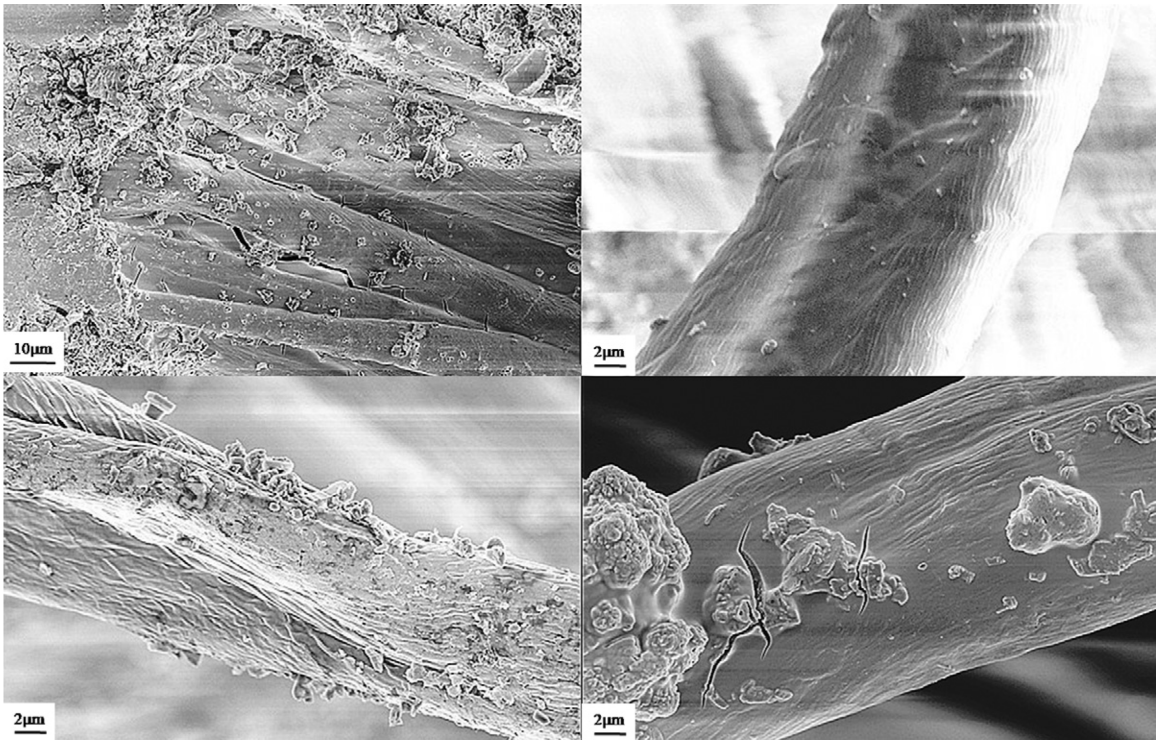


Fig. 7. FESEM magnifications of COT TMOS 15APMP.

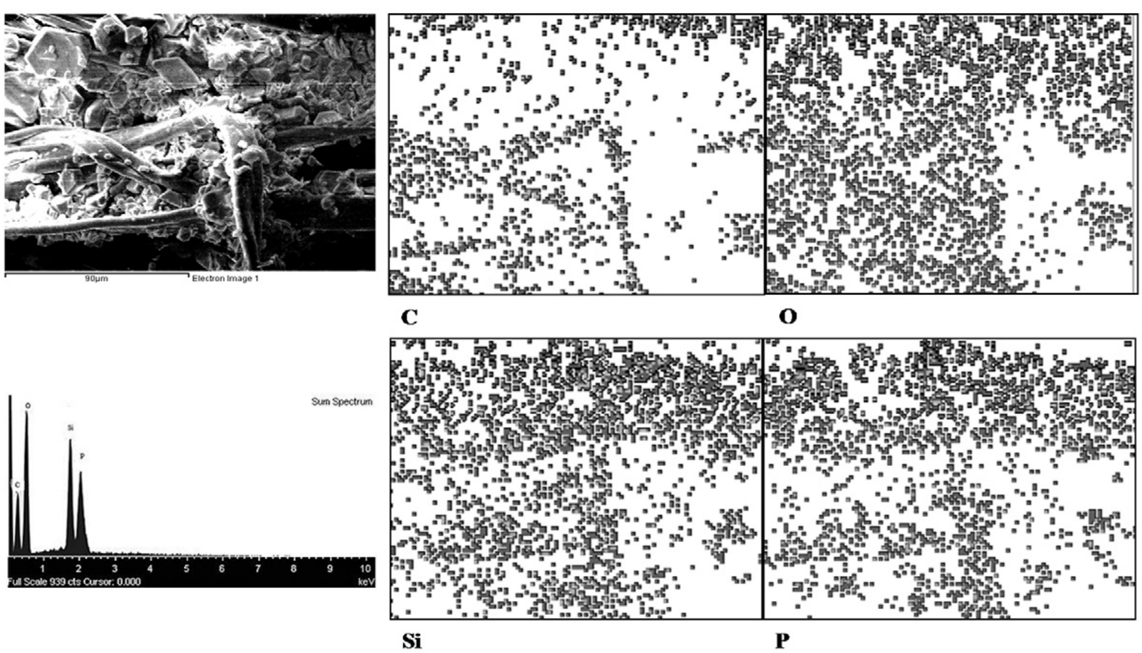


Fig. 8. EDS analysis of COT TMOS 15APMP and corresponding maps of Si and P elements.

3.4. Morphology

All the formulations containing phosphorus and silica show similar morphologies. Cotton fibers appear well covered by a compact silica coating, on which phosphorus aggregates are leant or included, as depicted for TMOS 15APMP in its FESEM magnifications (Fig. 7). In order to have a qualitative distribution of the two components on cotton fibers, elemental analysis (EDS) and Si and P mapping have been performed and plotted in Fig. 8: both the elements appear homogeneously distributed and finely dispersed onto cotton fibers in the corresponding maps; in addition, if Si and P element maps are superimposed, they almost completely overlap.

4. Conclusions

The sol–gel technique has been successfully coupled with the use of phosphorus-based compounds in order to enhance the flame retardancy of cotton fabrics. The possibility to get a synergistic effect of the two components has been investigated and demonstrated. To this aim, three different phosphorus compounds, namely aluminium phosphinate, a mix of aluminium phosphinate, melamine polyphosphate and zinc and boron oxide, and α-zirconium dihydrogen phosphate, have been considered. Cone calorimetry tests performed on cotton fabrics treated with aluminium phosphinate as model molecule have shown that high amounts of phosphorus compounds (30 and 50 wt.%, respectively) generate high concentrations of flat smokes. It was found that 5 and 15 wt.% are the most promising concentrations of phosphorus compounds with respect to sol–gel precursor to strongly improve the flame retardancy of cotton on the basis of a synergistic effect. Furthermore, it was demonstrated that the optimal methodology for combining the two species is to mix them during the sol preparation.

Flammability tests in vertical and horizontal configuration have pointed out that the strategy of performing a sol–gel treatment in the presence of suitable phosphorus compounds added to the sol solution allows to enhance the flame retardancy of cotton in remarkable way. This novel treatment turned out to be efficient also when the samples have been washed for 1 h at 60 °C in distilled water.

The thermo-oxidative stability in air of cotton was found to be strongly modified since the carbonization step is favoured by the synergistic effect of silica and phosphorus species, as evidenced by the final residues obtained. This effect can be ascribed to the high level of distribution and dispersion of phosphorus and silica on and in between the cotton fibers, as revealed by FESEM characterization.

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