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Sol–gel treatments on cotton fabrics for improving thermal and flame stability: Effect of the structure of the alkoxysilane precursor

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ABSTRACT

Sol–gel treatments have been performed on cotton fabrics in order to promote the formation of a surface silica insulating barrier, able to enhance their thermo-oxidative stability and flame retardancy. In particular, the role of several silica precursors, which differ as far as their structure (number and type of hydrolysable groups, presence of aromatic rings) is concerned, has been thoroughly investigated. The level of silica distribution and dispersion on and within the fabrics was found to depend on the type of precursor employed, as revealed by scanning electron microscopy and elemental analysis. All the precursors were able to favour the char formation in air below 360 °C, as stated by thermogravimetric analysis: in particular, the highest thermal stability was achieved in the presence of precursors bearing aromatic rings. Indeed, both flammability resistance and combustion behaviour of the treated fabrics were remarkably enhanced.

1. Introduction

It is well documented that nanometric fillers can significantly enhance the flame retardancy of polymers, since thermal degradation and combustion mechanism of the latter dramatically change in the presence of such additives (Horrocks, 2008; Jiang, 2010; Wilkie & Morgan, 2008). Scientists have hypothesized and proposed several action routes exerted by the nanofillers: in particular, it has been observed that a surface insulating barrier, which includes a high nanoparticle content, is formed upon pyrolysis and combustion of the polymer. Indeed, this barrier is thought to be responsible for improving flame retardancy (Lewin, 2006; Tang & Lewin, 2008). The most shared hypothesis on the formation of such a barrier in bulk nanocomposites lays on the migration of the nanoparticles on the surface, thus forming a continuous ceramic layer that prevents the heat and oxygen transfer from the ambient to the bulk polymer (Kashiwagi et al., 2000; Lewin, 2003, 2006; Tang & Lewin, 2008), as confirmed by XPS measurements (Schmitt & Gardella, 1986; Thomas & O'Malley, 1981).

These findings have been observed for the nanocomposites containing either natural or organo-modified phyllosilicates (clays) or silica. For this latter system, Kashiwagi et al. (2000) have investigated the effect of silica particles added to polypropylene and polyethylene oxide by melt blending and studied their flame retardant efficiency as well as kinetics and mechanism. It was found that the kinetics relies on a physical effect (instead of a chemical "driving force"), due to the silica segregation within the outermost polymer layers, which provides thermal insulation against the degradation of the volatile products moving from the polymer to the surface. Furthermore, cone calorimetry data (heat release and mass loss rate) have demonstrated that the silica synthesized through sol–gel processes (i.e. by means of a bottom-up approach) is more efficient than fumed and fused silica submicro- and nanoparticles, probably because of a better control of their size and distribution.

The use of sol–gel processes for obtaining silica nanoparticles is well documented in the literature. Several papers have recently investigated the possibility to reduce the flammability of different polymers, such as epoxies (Chiang & Chang, 2008; Chiang & Ma, 2002; Chiang, Wang, Ma, & Chang, 2002; Hsiue, Liu, & Liao, 2001; Liu & Chou, 2005; Liu, Wu, Chiu, & Ho, 2003; Yu, Liu, & Liu, 2010) and phenolic resins (Chiang & Ma, 2004; Chiang, Ma, Wu, & Kuan, 2003), polymethylmethacrylates (Chiang & Chiu, 2009; Messori et al., 2003), polyesters (Ji, Wang, Zhang, Kong, & Xia, 2009) and polyimides (Liu, Gao, Wang, Li, & Xu, 2002), by exploiting silica phases derived from sol–gel processes. Therefore, since silica coatings can be extremely efficient as insulating barrier on the surface of any substrate and in particular on fabrics, we recently focused on the use of sol–gel treatments performed on cotton fabrics.

We have already demonstrated that two common silica precursors, namely tetramethylorthosilicate and tetraethylorthosilicate, are effectively suitable for enhancing the flame retardant properties of cotton fabrics (Alongi, Ciobanu, Carosio, Tata, & Malucelli,

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2011; Alongi, Ciobanu, & Malucelli, 2011a, 2011b, 2011c). Nevertheless, such investigation has never been extended to assess the effectiveness of several commercially available alkoxysilanes, which differ in their chemical structure (i.e. number and type of hydrolysable groups, possible presence of aromatic rings in their backbone). Therefore, in the present paper we present a systematic investigation on the structure-property relationships of cotton fabrics treated with these silica precursors. The effects of both the chemical structure of the used alkoxides and the morphology of the silica phases formed after the sol–gel treatment on the thermo-oxidative stability, flammability and combustion behaviour of the treated fabrics are deeply investigated.

2. Experimental part

2.1. Materials

Cotton fabrics (CO, purchased from Fratelli Ballesio, Torino, Italy) with a density of 200 g/m^2 were used as received. Several silica precursors (the structure of which is schematized in Table 1), water, ethanol and dibutyltindiacetate—DBTA, (all reagent grade) were purchased from Sigma–Aldrich and used without any further purification.

2.2. Sol–gel treatments on the cotton fabrics

Pure silica phases were synthesized on the cotton fabrics through sol–gel processes. More specifically, a mixture containing the precursor, distilled water (precursor: water molar ratio = 1:1), ethanol and DBTA (0.9 wt.%) was stirred at room temperature for 10 min. Then, 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. Finally, all the fabrics were washed for 1 h in distilled water at 60 °C in order to eliminate the unreacted precursor.

Hereinafter, the treated cotton samples will be identified by using the code of the inorganic precursor, as reported in Table 1.

2.3. Characterization techniques

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 (ca. 10 mg), in air atmosphere (60 ml/min). Further tests were performed by treating the fabrics in a muffle at 1100 °C for 1 h.

The flame retardancy properties of the prepared samples were measured through flammability and combustion tests. As already reported, such tests are complementary in order to entirely describe a realistic fire scenario (Alongi et al., 2011b).

The flammability test in vertical configuration was carried out by applying a propane flame for 5 s at the centre of a fabric specimen (50 mm × 100 mm) and repeating the application for at least two times: this configuration allows to test the fabrics in the most drastic way. The test was repeated 5 times for each formulation, measuring burning time and rate and the final residue as well. This test aims to mimic the procedure described in ISO15025 standard, commonly employed for the protective garments, although the specimen size used in this work is smaller (100 mm × 20 mm *vs*. 200 mm × 16 mm in ISO15025).

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 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) and effective heat of combustion (EHC, MJ/kg) 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), carbon monoxide and dioxide yield ([carbon monoxide] and [carbon dioxide], kg/kg, respectively) were also evaluated. For each sample, the experiments were repeated four times in order to ensure reproducible and significant data. The experimental error was within 5%.

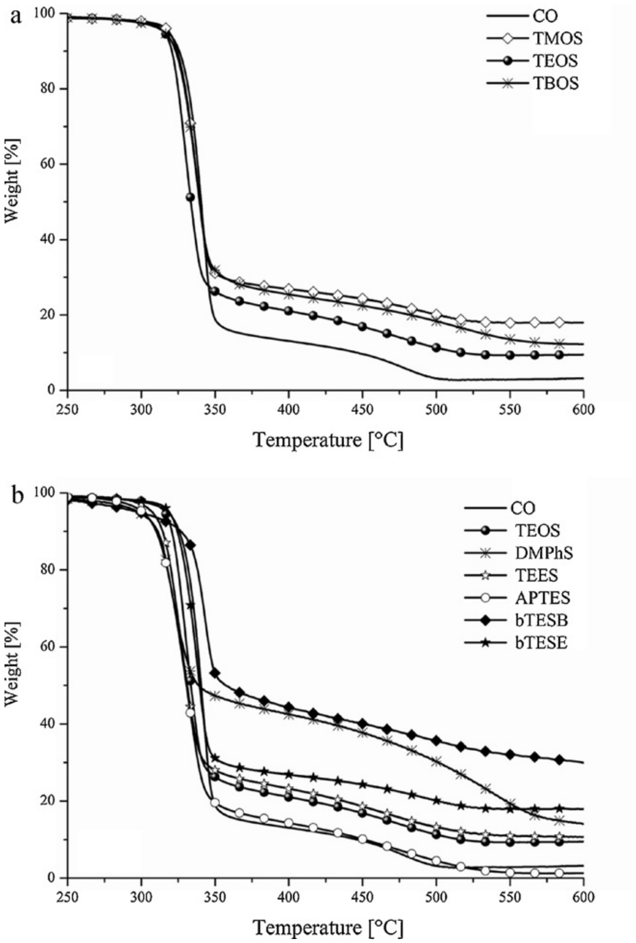


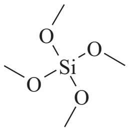
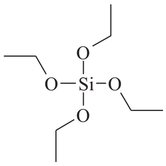
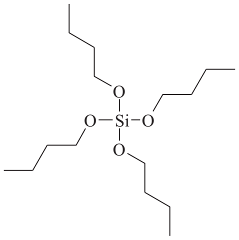
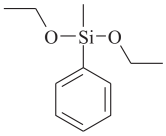
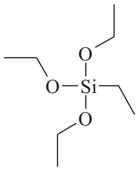
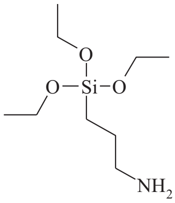
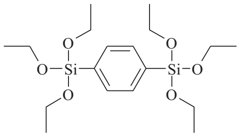
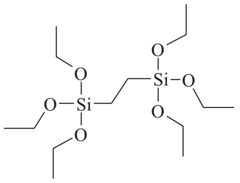
Fig. 1. TG curves of the fabrics in air.

Since water can significantly influence the combustion behaviour of such a polar fabric as cotton, the water content was measured by using a Karl–Fisher titrator (Mettler Toledo, model V20). Fabric pieces (ca. 1 g) were heated up to 100 °C and the water content was established using a mixture of methanol, potassium metabisulphite and I$_2$ as titration system.

All Magic Angle Spinning (MAS) solid-state NMR spectra were acquired on a Bruker Advance III 500 spectrometer with a wide bore 11.7 Tesla magnet and operational frequencies for ^{29}Si of 99.35 MHz in HPDEC conditions. A 7 mm robe with MAS was employed in all the experiments. The samples were packed on a Zirconia rotor and spun at 5000 Hz.

The surface morphology of the treated samples was studied using a LEO-1450VP Scanning Electron Microscope, equipped with a X-ray probe (INCA Energy Oxford, Cu-K$_\alpha$ X-ray source,

Table 1
Silica precursors.

Name	Code	Number and type of alkoxy functionalities	Chemical formula
Tetramethylorthosilicate	TMOS	4 (methoxy)	
Tetraethylorthosilicate	TEOS	4 (ethoxy)	
Tetrabuthylorthosilicate	TBOS	4 (buthoxy)	
Diethoxy(methyl)phenylsilane	DEMPhS	2 (ethoxy)	
Triethoxy(ethyl)silane	TEES	3 (ethoxy)	
3-Aminopropyl triethoxysilane	APTES	3 (ethoxy)	
1,4-Bis(triethoxysilyl)benzene	bTESB	6 (ethoxy)	
1,2-Bis(triethoxysilyl)ethane	bTESE	6 (ethoxy)	

$k = 1.540562$ Å), which 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.

3. Results and discussion

3.1. Thermal stability in air

We have already demonstrated that the sol–gel process does not change the thermal stability of cotton in nitrogen in remarkable way, whereas the degradation mechanism in air is strongly influenced by the presence of silica phases (Alongi, Ciobanu, Carosio, et al., 2011; Alongi et al., 2011a, 2011b, 2011c). Indeed, silica, acting as physical barrier, is able to protect the cotton from the heat and oxygen and favour the formation of a carbonaceous residue, also at low temperatures. Cotton degradation is a two-step reaction, which involves the decomposition of the glycosyl units to char at low temperatures (ca. 350 °C) and subsequently the depolymerization of such units to volatile products containing levoglucosan at higher temperatures (ca. 500 °C).

Table 2
TGA data in air and residues after thermal treatment at 1100 °C for 1 h.

Sample	$T_{\max1}$[a] [°C]	$T_{\max2}$[a] [°C]	Residue at 360 °C [%]	Residue at 500 °C [%]	Residue at 750 °C [%]	Residue at 1100 °C in muffle [%]
CO	342	484	16	3	3	<1
TMOS	338	496	29	20	20	20
TEOS	331	485	26	11	10	7
TBOS	338	495	29	18	12	6
DEMPhS	321	546	46	30	11	5
TEES	327	471	26	13	10	5
APTES	332	475	17	4	2	1
bTESB	343	–	49	36	23	16
bTESE	339	497	29	20	18	18

[a] From derivative curves.

All the investigated alkoxysilanes substantially favour the char formation, as reported in Table 2 that collects the residues in air at 360, 500 and 750 °C. The degradation mechanism is not influenced in a significant manner; indeed, the degradation profiles are similar to that of neat cotton (Fig. 1a and b). This finding was further confirmed by testing the treated fabrics at 1100 °C for 1 h in a muffle (Table 2, last column); in addition, Fig. 2 depicts the residue of all the treated fabrics after this test.

Comparing TMOS, TEOS and TBOS (Fig. 1a), which have the same number of hydrolysable groups, but different alkoxy chain length (namely, tetramethoxy, tetraethoxy and tetrabutoxy chains), it is possible to notice that TMOS gives the highest residue. This residue appears dense and compact, as observed in Fig. 2 and the original texture of the fabric is still distinguishable.

The explanation of such a different behaviour among the precursors can be attributed to differences in the kinetics of hydrolysis and of the subsequent condensation step. Indeed, as reported in the literature, TEOS is able to give hydrolysis before TMOS in acidic conditions (as well as in alcoholic solutions) and, thus, to form silica as soon as a condensation catalyst (DBTA) is added (Cihlar, 1993). Thus, we have compared the behaviour of two alcoholic TMOS and TEOS solutions prepared with and without the condensation catalyst (Fig. 3a). Fig. 3a shows two test tubes completely transparent in the absence of DBTA for both precursors. When DBTA is added, TMOS forms a transparent solution, while TEOS immediately gives rise to a white/milky gel. This means that, silica is already forming in TEOS solution since it hydrolyses more quickly than TMOS. For this reason, when a fabric is treated in a TMOS solution (containing the condensation catalyst), this precursor has time to be significantly adsorbed within the fabric texture and subsequently it starts to form the silica network directly onto the fiber surface during the further thermal treatment. On the other hand, by treating the cotton fabric with TEOS + DBTA, part of the precursor has already reacted, thus it cannot be efficiently uploaded by the fabric and exploited during the thermal treatment for the formation of the silica layer. These findings substantially agree with the residues obtained by thermogravimetric analyses (Table 2).

Furthermore, the ethoxy-based precursors (TEOS, TEES and DEMPhS) show a 10-fold final residue at 750 °C with respect to neat cotton, regardless of the different number of hydrolysable groups (4, 3 and 2, respectively), as reported in Fig. 1b and Table 2.

Also APTES that bears an amino group, has been tested: the obtained results show that such alkoxysilane is not efficient for improving the cotton thermal stability in air: indeed, the TGA curves of APTES and cotton are practically overlapped (Fig. 1b). In addition, APTES, similarly to cotton, does not leave a significant residue at 1100 °C (Fig. 2). More specifically, comparing TEES and APTES precursors firstly, it is possible to observe that only TEOS is able to protect cotton from thermal degradation in air, because of the lower ethoxy functionality of APTES, so that the formation of silica phases is probably slowed down. Indeed, the final residue of the APTES system at high temperature (i.e. 750 °C) is comparable to cotton within the experimental error of the test.

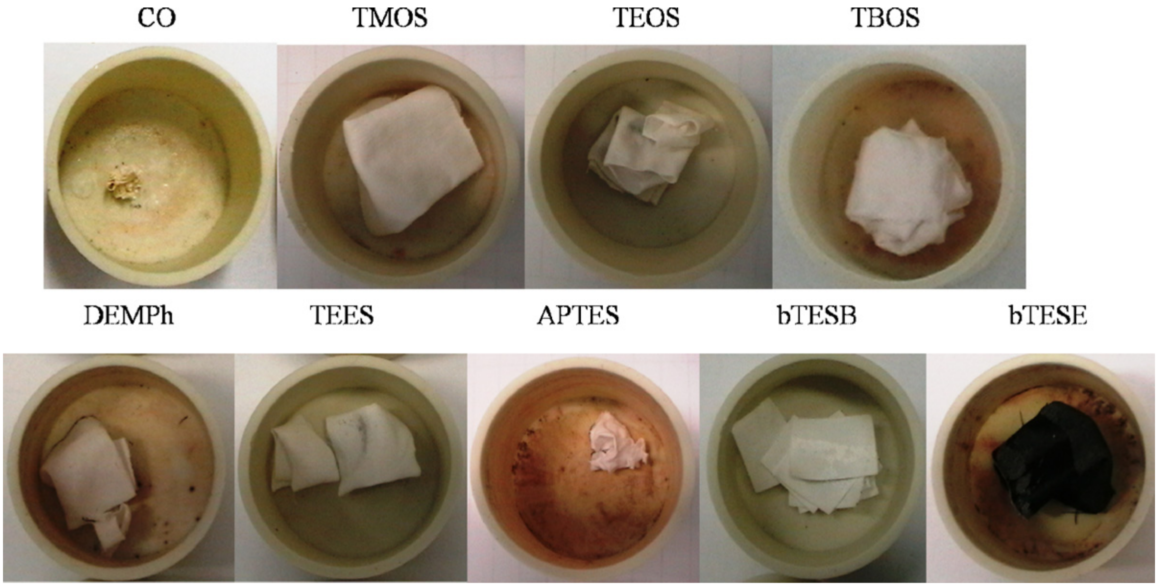


Fig. 2. Fabric residues after a thermal treatment in muffle for 1 h at 1100 °C.

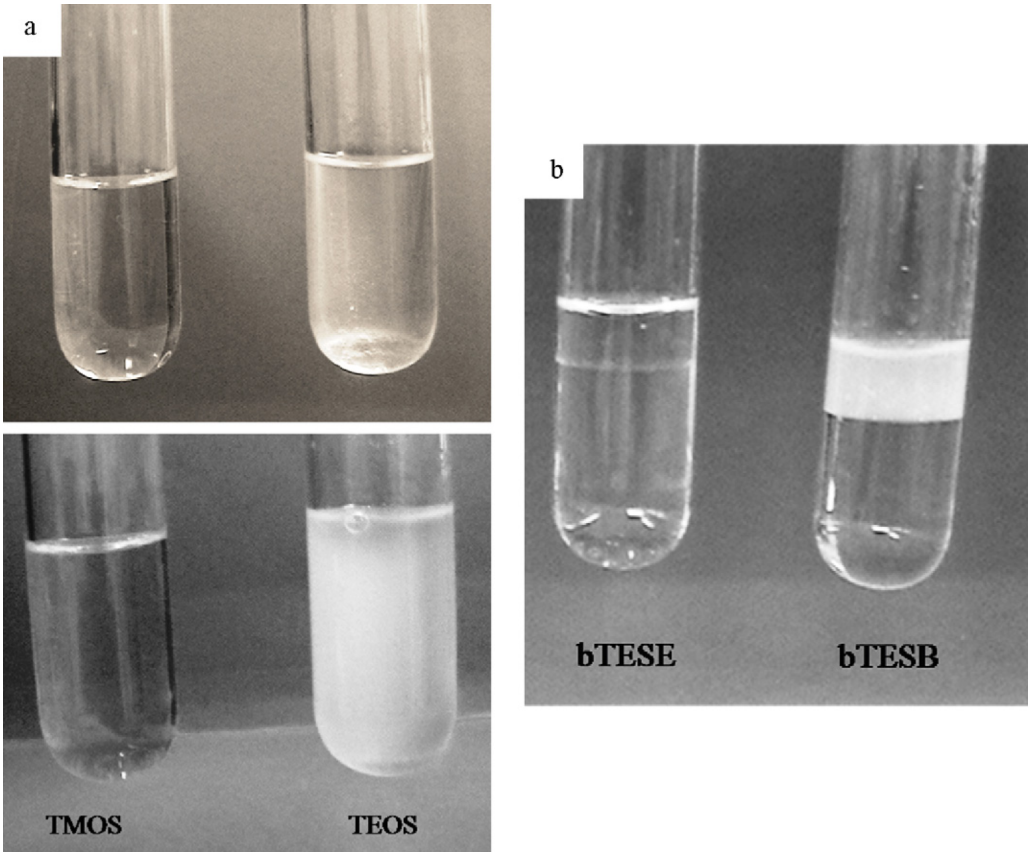


Fig. 3. Test tubes containing TMOS and TEOS (a) and bTESE and bTESB (b) alcoholic solutions.

Furthermore, high residues at 750 °C are achieved for the precursors bearing the highest number (6) of hydrolysable groups, i.e. for bTESB (23%) and bTESE (18%): a more uniform silica network is probably formed because of their high functionality. Furthermore, the presence of an aromatic ring in bTESB promotes carbonisation phenomena, thus leading to a higher residue with respect to the analogous aliphatic precursor (bTESE). Such behaviour was further confirmed by testing the treated fabrics at 1100 °C for 1 h in a muffle (Fig. 2 and Table 2).

On the basis of the above results, it is possible to rank the precursors (from the most to the less efficient at high temperature), on the basis of the protective role exerted on cotton thermal stability:

TMOS > bTESB > bTESE > TEOS > TBOS ≈ TEES ≈ DEMPhS > APTES

3.2. Flammability

As already demonstrated, the sol–gel process is a useful method to enhance the flame retardancy of synthetic and natural textile substrates. In particular, tetramethyl- and tetraethyl-orthosilicates were found to significantly improve the thermal stability and combustion behaviour of cotton (Alongi, Ciobanu, Carosio, et al., 2011; Alongi et al., 2011a, 2011b, 2011c).

In the present work, the fabrics treated with TMOS, TEOS and TBOS precursors have shown an ameliorated resistance to a direct flame, as evidenced in Table 3 by the increasing number of flame applications that are necessary to burn the specimens. In addition, the total burning time is significantly increased, the burning rate remarkably decreased and the final residue after the test is higher than that of neat cotton. Indeed, cotton burns rapidly with a bright fire without leaving any residue, whereas the TMOS, TEOS and TBOS treated fabrics start to burn as soon as the flame is applied, then the flame burns out and the combustion proceeds by a glow front that reaches the bottom of the specimen very slowly, leaving a significant final residue (48%, 35% and 33% for TMOS, TEOS and TBOS, respectively, Fig. 4). Furthermore, comparing the performances of cotton, TMOS, TEOS and TBOS, it is possible to conclude that all precursors are efficient flame retardants and TMOS is slightly more effective than TEOS and TBOS (Table 3).

In conclusion, being equal the number of hydrolysable groups (4), the shorter is the chain length of the silane precursor, the lower is the flammability of the treated cotton fabrics.

The influence of the number of hydrolysable groups of the precursors on the flammability of cotton has been also investigated. Table 3 collects the obtained data and Fig. 4 plots some typical pictures of the fabrics during and after the flame application(s).

Table 3
Flammability tests.

Sample	Number of flame applications	Total burning time [s]	Total rate [mm/s]	Residue [%]
CO	1	40	2.50	10
TMOS	2	70	1.43	48
TEOS	2	57	1.75	35
TBOS	2	57	1.75	33
DEMPhS	2	55	1.81	30
TEES	2	55	1.81	31
APTES	2	50	2.00	20
bTESB	10/2[a]	77	1.70	96/41[a]
bTESE	2	69	1.45	20

[a] Half the tested samples required 10 flame applications and exhibited 96% residue.

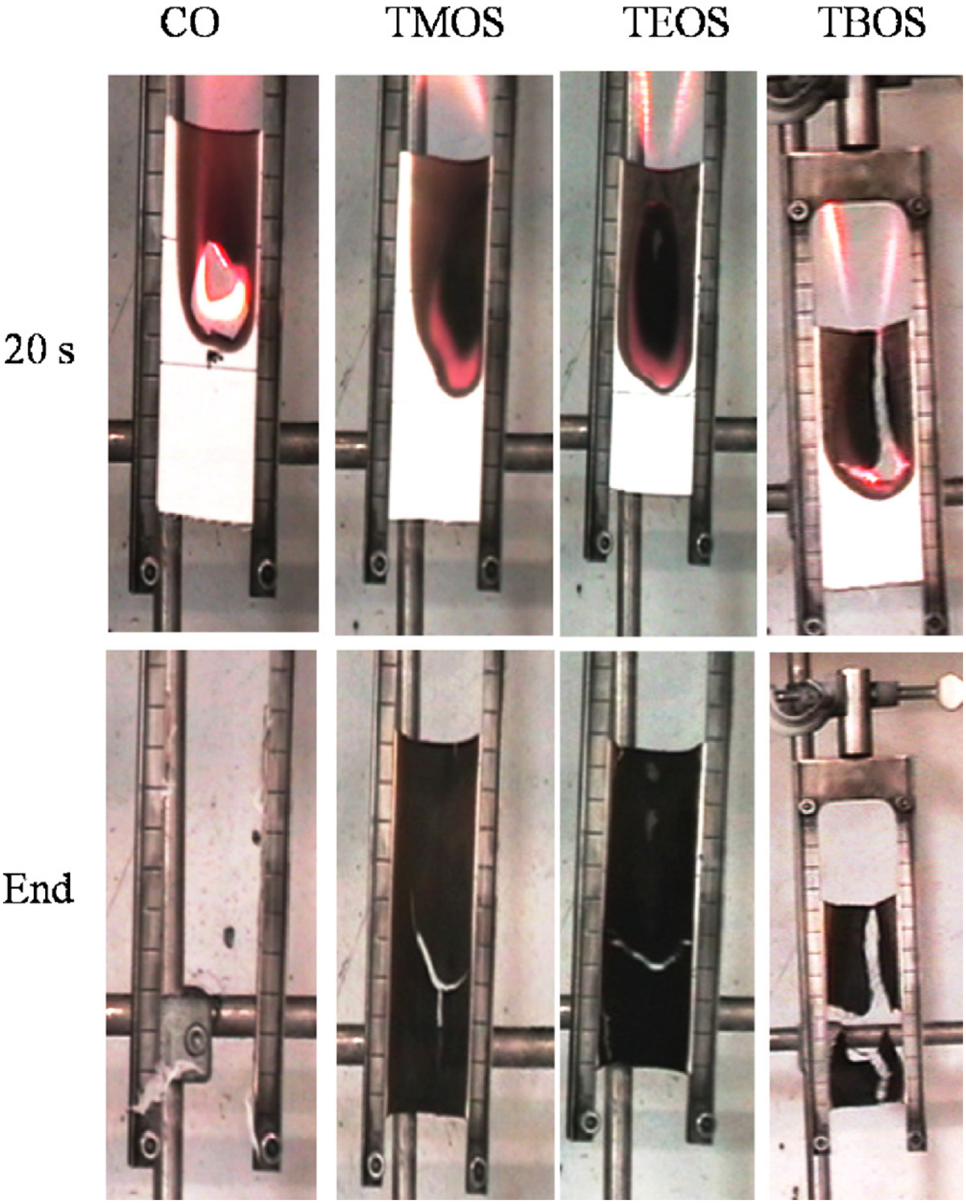


Fig. 4. Fabric residues after flammability test.

Referring to DEMPhS and TEES precursors (analogous to TEOS), a general improvement of the cotton flame retardancy can be observed (Table 3). More specifically, although DEMPhS and TEES bear a lower number of hydrolysable groups (i.e. 2 and 3, respectively), they show a flammability behaviour similar to that of TEOS, with the only exception of the huge smoke release for DEMPhS and the aspect of their final residue (shrunk, not dense, not compact and very thin). As a matter of fact, their solutions evidence

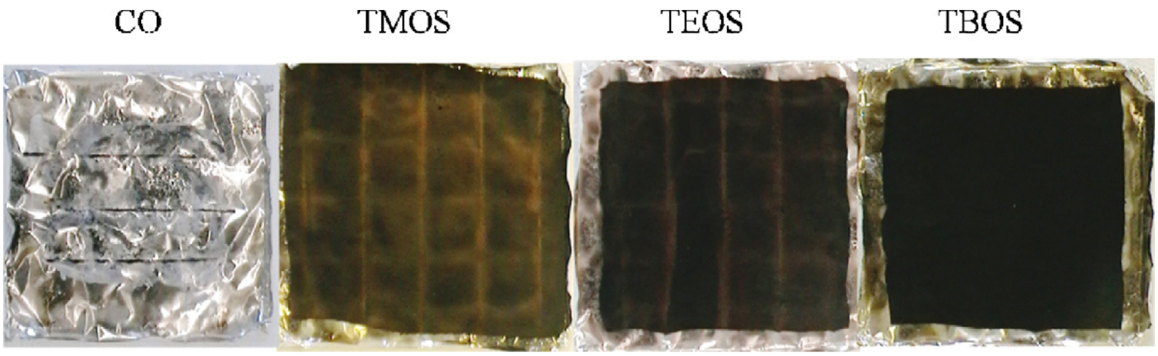


Fig. 5. Fabric residues after combustion test.

Table 4
Cone calorimetry data.

Sample	TTI [s]	pkHRR [kW/m^2]	FPI [s m^2/kW]	THR [MJ/m^2]	EHC [MJ/kg]	TSR [m^2/m^2]	SEA [m^2/kg]	[Carbon monoxide] yield [kg/kg]	[Carbon dioxide] yield [kg/kg]	Water amount [ppm][a]
CO	20	91	0.22	2.8	15.4	38	27	0.0287	2.61	46.000
TMOS	30	82	0.37	1.8	12.8	31	19	0.0199	2.46	59.100
TEOS	30	85	0.35	2.3	14.4	33	15	0.0135	2.51	60.600
TBOS	28	90	0.31	2.2	14.8	33	17	0.0153	2.54	50.100
APTES	18	103	0.18	2.6	15.0	26	23	0.0545	2.68	41.400
TEES	19	90	0.21	2.6	15.3	27	31	0.0454	2.66	45.700

[a] By Karl–Fisher titration.

the quick formation of a gel after the addition of the condensation catalyst, as previously described for TEOS precursor. Thus, also in this case, the key factor of the flammability performances is strictly related to the initial hydrolysis kinetics.

Even though APTES precursor is able to slightly enhance the flame retardancy of cotton (Table 3) too, its effectiveness is lower than TEES, as evidenced by the final residues after the test (20% *vs.* 31%). In addition, TEES generates a compact and thick residue, whereas a transparent and thin film is formed when APTES is used. Once again, the lower efficiency of APTES precursor with respect to TEOS can be ascribed to the sol–gel process kinetics. Indeed, the gel point is not quickly reached during the impregnation of the fabric by APTES solution, since this precursor has a lower alkoxy functionality than TEOS, but only during the subsequent thermal treatment. Therefore the silica network formation is not favoured, as evidenced by thermogravimetric analyses (Figs. 1b and 2 and Table 2).

By increasing the number of hydrolysable groups (bTESB and bTESE), the flammability behaviour completely changes: indeed, the fabric treated with bTESB precursor is the most performing since 10 flame applications are not enough to burn the specimen. Nevertheless, this behaviour has been observed for half the tested specimens on 6 (3 of 6, the other specimens behave like TEOS). Such results suggest that the sol–gel process carried out in these experimental conditions is not probably complete and thus some non-reacted species are still present, despite the washing treatment in water. Thus, solid state ^{29}Si-NMR analysis has been exploited for assessing the degree of condensation of the different precursors on cotton fabrics (*see* below).

bTESE still behaves better that neat cotton, but much worse than bTESB, as shown in Table 3. These results can be ascribed to the initial hydrolysis kinetics, well depicted in Fig. 3b: indeed, for bTESE, a phase separation between the precursor and the alcoholic solution occurs, thus slowing down the silica formation. On the contrary, as already described for TEOS, the hydrolysis reaction of bTESB starts immediately when DBTA is added to the alcoholic solution (Fig. 3b): as a matter of fact, such two precursors show comparable silica amounts (Table 2, last column).

Finally, the presence of a benzene ring in bTESB structure contributes to the formation of a polycondensed carbonaceous residue, which may decrease the flammability of the treated fabrics.

Also for flammability tests, it is possible to establish a ranking of the precursors (from the most to the less efficient) as function of the protective role that they are able to play on cotton:

bTESB >> TMOS > TEOS ≈ TBOS ≈ TEES ≈ DEMPhS > bTESE > APTES

3.3. Combustion behaviour

The combustion behaviour of the neat cotton and of the sol–gel treated fabrics has been investigated by cone calorimetry; the obtained data are collected in Table 4.

Both TMOS and TEOS precursors are able to increase the TTI (30 *vs.* 20 s) of cotton and slightly decrease THR (1.8 and 2.3 *vs.* 2.8 MJ/m^2), EHC (12.8 and 14.4 *vs.* 15.4 MJ/kg) and the combustion kinetics in terms of pkHRR (82 and 85 *vs.* 91 kW/m^2). Thus, the corresponding FPI values are higher than that of the neat fabric (0.37 and 0.35 *vs.* 0.20 s m^2/kW). This trend is similar to that observed for the flammability tests and can be ascribed to the presence of the silica layer that, acting as physical barrier, is able to protect cotton from heat and oxygen transfer. Indeed, at the end of the combustion, the final residue is still dense and compact, as is clearly observable in Fig. 5. Such improvements can be also attributed to the high water content determined for TEOS and TMOS treated fabrics, which can favour the TTI and FPI increase and THR decrease

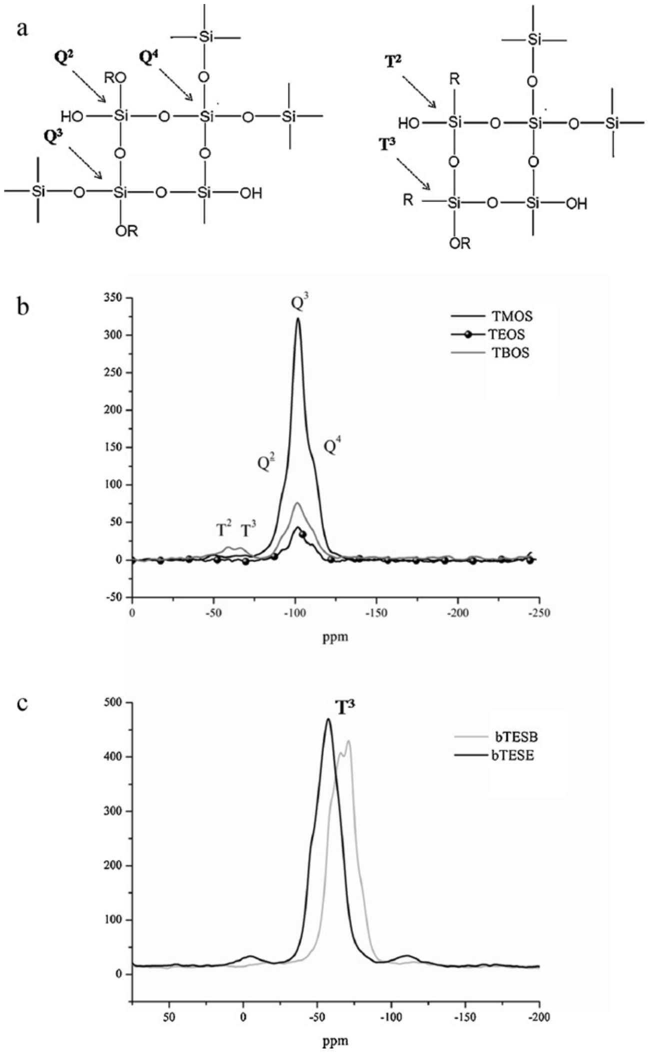


Fig. 6. Solid state ^{29}Si-NMR spectra of the treated fabrics.

Table 5
Frequency of the different Q and T species in the sol–gel treated fabrics from ^{29}Si-NMR spectra.

Sample	Frequency (ppm)						
	Q^1	Q^2	Q^3	Q^4	T^1	T^2	T^3
TMOS	–	−92	−101	−110	–	–	–
TEOS	–	−92	−101	−110	–	–	–
TBOS	–	−92	−101	−110	–	−59	−66
DEMPhS					−34	−60	−66
TEES	–	–	–	–	−34	−59	−66
APTES	–	–	–	–	−30	−59	–
bTESB	–	–	–	–	–	–	−66/71
bTESE	–	–	–	–	–	–	−66

(Table 4, last column). As far as the produced smokes are considered, both TMOS and TEOS precursors are responsible of TSR and SEA decrease, as well as of low mono and dioxide evolution during the combustion. Once again, this effect is due to the water content of the fabrics that is able to dilute the produced smokes and their optical density (indirectly measured by SEA).

TBOS performances are comparable to TMOS and TEOS in terms of TTI increase, but not as far as the pkHRR decrease is concerned (Table 4).

APTES performances are lower than TEOS and even than cotton (APTES FPI is 0.18 *vs.* 0.35 and 0.22 s m^2/kW of TEOS and cotton, respectively). Indeed, TTI is practically unchanged (within the experimental error), whereas THR, EHC and pkHRR are higher than neat cotton, probably because of the lower water content (41.400 *vs.* 60.600 ppm) and the presence of the non-hydrolysable organic part (i.e. the aminopropyl chain) that decomposes. Furthermore, the silica coating formed on the cotton surface is extremely thin and not dense, therefore, during the combustion, it breaks in some areas, thus creating preferential channels, in which the gases are concentrated and can leak out. All these hypotheses could explain the observed pkHRR increase. At the end of the combustion, the fabric does not maintain its texture, since the silica content is low and not capable to protect cotton, in agreement with the TGA results.

Referring to smokes, it is interesting to notice that the carbon monoxide and dioxide production is higher than that of cotton: this effect is due to the non-hydrolysable organic part that decomposes at high temperatures to carbon monoxide and subsequently to carbon dioxide.

TEES turns out to be a better insulator than APTES, since the silica coating is more consistent, even though less dense than TEOS. Indeed, the FPI of TEES is lower than TEOS, 0.21 *vs.* 0.35 s m^2/kW. As for APTES, carbon monoxide and dioxide production is induced by decomposition of the non-hydrolysable organic part (ethyl chain).

Finally, cone calorimeter data of cotton fabrics treated with DEMPhS, bTESB and bTESE seem to be not significant and reproducible. The high variance can be ascribed to the sol–gel chemistry involved, which probably continues during the irradiation under the cone, favouring a further silica formation. Thus, the silica coating cannot play a protective role during the combustion of cotton since it is still forming. This result seems to confirm the flammability behaviour of the samples treated with bTESB. On the other hand, flammability tests are not influenced by the incompleteness of the sol–gel processes: indeed, when a flame is directly applied to the fabrics, the presence of even a low amount of silica is able to burn out the flame and slow down the cotton burning.

3.4. Solid state ^{29}Si-NMR analyses

In order to better explain the flame retardancy properties of the fabrics treated with the different inorganic precursors, the degree of alkoxysilane condensation has been evaluated by solid-state ^{29}Si-NMR spectroscopy.

TMOS, TEOS and TBOS give similar spectra, which show three signals at approximately −90, −100 and −110 ppm, attributable to Q^2, Q^3 and Q^4 structures, respectively (Table 5, Fig. 6a and b). The proportions of the Q species present in the system have been extracted from the ^{29}Si-NMR spectra using a standard Gaussian line-shape deconvolution technique based on the peak areas of each species (Yu, Chen, & Chen, 2003). The results indicate that the condensation is always incomplete, regardless of the precursor type: 77.5% and 82.2% for TMOS and TEOS, respectively. For TBOS, this calculation has not been performed because of the presence of T^2 and T^3 structures due to the unreacted precursor (Fig. 6b). The ^{29}Si-NMR spectra show that the sol–gel treated fabrics are mainly cross-linked by Q^3 species. Indeed, if the systems were fully condensed, only Q^4 species would appear.

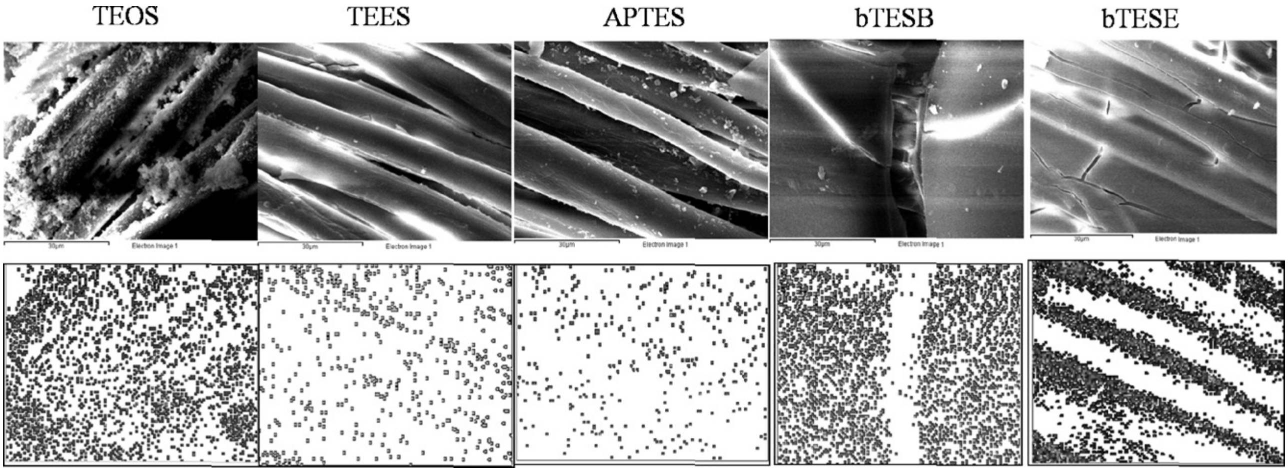


Fig. 7. SEM magnifications and Si maps of the treated fabrics.

As far as DEMPh, TEES and APTES are considered, it is worth to notice that no Q, but only T structures appear: this means that only a partial crosslinking occurs, not able enough to create an oxide network for completely protecting the cotton fabrics as for TMOS, TEOS and TBOS during the thermo-oxidation or combustion.

Similarly, the presence of T^2 and T^3 species for bTESB and bTESE (hexafunctional precursors), suggests that such systems are not completely condensed, thus determining the high variance observed in the flammability and cone calorimetry tests (Table 5, Fig. 6c).

3.5. Morphology of the treated fabrics

In order to establish a correlation between the observed flame retardancy properties of the treated fabrics and the distribution of silica on the fibers, the morphology of these samples has been studied through scanning electron microscopy. The level of silica distribution and dispersion on the fabrics depends on the type of precursor employed: indeed, as shown in Fig. 7 (micrographs and Si mapping), the fabrics treated by TEES and APTES show a weak Si distribution on the fibers as compared to that found for TEOS. For TMOS and hexafunctional precursors, the dispersion level of the silica is high, although its distribution is not very homogeneous; in addition, bTESB and bTESE fabrics show the presence of some cracks on the silica coating.

In conclusion, the fabrics with the best performances in terms of flammability and combustion tests (TMOS, TEOS and TBOS) are those characterized by high amounts of silica well-homogeneously distributed on the fibers.

4. Conclusions

Cotton fabrics were sol–gel treated with several alkoxy precursors, having a different number and type of hydrolysable groups and in some cases bearing aromatic rings in their backbone, in order to investigate their thermo-oxidative stability, flammability and combustion behaviour.

The effectiveness in improving cotton fire resistance was found to depend on both the type of the used alkoxysilane and its reactivity during the sol–gel processes. Solid-state ^{29}Si-NMR spectroscopy indicated that the condensation is always incomplete, regardless of the used alkoxysilane; the level of incompleteness was found to affect the combustion behaviour of the treated fabrics.

Scanning electron microscopy showed a good and homogeneous distribution of silica when cotton fabrics were treated with TMOS, TEOS and TBOS; such alkoxysilanes were also found to strongly reduce the flammability and to enhance the fire performances of cotton. All the investigated precursors favoured the char formation in air below 360 °C, as stated by thermogravimetric analysis, and the presence of aromatic rings allowed to achieve the highest thermo-oxidative stability.

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