Carbohydrate Polymers 87 (2012) 2093–2099

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Thermal stability, flame retardancy and mechanical properties of cotton fabrics treated with inorganic coatings synthesized through sol–gel processes

Jenny Alongi*, Mihaela Ciobanu, Giulio Malucelli

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

ARTICLE INFO

Article history:
Received 29 August 2011
Received in revised form 11 October 2011
Accepted 14 October 2011
Available online 20 October 2011

Keywords:
Cotton
Sol–gel processes
Flame retardancy
Mechanical properties, abrasion resistance

ABSTRACT

Cotton was sol–gel treated employing several metal alkoxide precursors (namely, tetraethylorthosilicate, -titanate, -zirconate and aluminium isopropylate) in order to get inorganic phases able to improve the thermal stability and flame retardancy of the fabric, without changing its mechanical features. Indeed, after the sol–gel treatment the fibre/fabric surface was morphologically modified: a homogeneous and compact film located in the fibre interstices (warp and weft) and partially covering their walls was observed for all the systems investigated. These coatings turned out to be responsible of an overall enhancement of the thermal and fire stability of the fabrics preserving, at the same time, the original mechanical properties of the neat cotton in terms of tensile strength and deformation. In addition, such inorganic coatings increased the abrasion resistance of the cotton in a remarkable way.

1. Introduction

In the last two decades, the growing global competition has led both the academic and industrial research activities toward novel applications and innovatory solutions in the textile field in order to confer a high-added value to such traditional materials as cotton, polyester and polyamide. The possibility of imparting multifunctional features to a fabric represents one of the main goals that the researchers aim to achieve.

Several recent papers have demonstrated that it is possible to improve cotton features like water repellency (Kathiervelu, 2003; Russell, 2002), antimicrobial (Burniston, Bygott, & Stratton, 2004; Daoud & Xin, 2004) and UV protection (Xin, Daoud, & Kong, 2004; Yang, Zhu, & Pan, 2003), antistaticity (Dong & Huang, 2002; Nie, Yu, Yu, Chen, & Gu, 2002; Wang & Chen, 2005), mechanical properties (Rosace, Canton, & Colleoni, 2010), thermal stability (Price, Horrocks, Akalin, & Faroq, 1997) and flame retardancy (Cireli et al., 2007; Lecoeur, Vroman, Bourbigot, Lam, & Delobel, 2001), by using different approaches, although with some limitations, particularly when referring to the washing resistance of the treated fibres/fabrics.

The above limitation can be substantially overcome using the sol–gel approach that represents a versatile synthetic route based on a two-step (hydrolysis and condensation) reaction, starting from (semi)metal alkoxides: thus, the formation of either inorganic micro/nano phases or hybrid organic–inorganic structures is achieved (Alongi, Ciobanu, & Malucelli, 2011a; Sakka, 2003).Such phases, which can be organized in form of (micro or nano) particles or coatings, have already shown to be able to protect the polymer surface from combustion by forming a physical barrier toward heat and oxygen diffusion, acting as insulators (Alongi, Ciobanu, Carosio, Tata, & Malucelli, 2011).

As is well described in the literature, it is possible to form sol–gel derived phases with tailored properties. Indeed, recently cotton fabrics have been treated with sol–gel titania hydrosols in order to improve their UV radiation protection (Abidi, Hequet, Tarimala, & Dai, 2007), self-cleaning and flame retardancy (Moafi, Shojaie, & Zanjanchi, 2011a). Analogously, coatings based on zirconia and alumina have been employed for enhancing the self-cleaning of cotton and wool fibres (Moafi, Shojaie, & Zanjanchi, 2010; Moafi, Shojaie, & Zanjanchi, 2011b) and wettability of polyester fabrics (Xiao, Chen, Wei, & Wu, 2009). Furthermore, our previous studies clearly demonstrated that alkoxysilane precursors can be used as efficient flame retardants for polyester (Alongi, Ciobanu, Carosio, et al., 2011), cotton (Alongi, Ciobanu, Carosio, et al., 2011; Alongi et al., 2011a; Alongi, Ciobanu, & Malucelli, 2011b; Alongi, Ciobanu, & Malucelli, 2011c; Alongi, Ciobanu, & Malucelli, in press) and blends of these fabrics (Alongi, Ciobanu, Carosio, et al., 2011).

In spite of these achievements, when the sol–gel method is applied to the synthesis of chemical finishes for textiles, the modification of fibre surface properties may lead to some drawbacks, such as yellowing or decrease of the fabric tensile strength, thus limiting the possible application of these materials (Mahltig & Fischer, 2010; Rosace et al., 2010; Wong & Aziz, 2007).

---

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

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.10.032

Although many efforts have been carried out, to our best knowledge a detailed study on the effectiveness of inorganic coatings derived from different metal alkoxides has not yet been assessed with the aim of enhancing the thermal and fire stability, as well as preserving (or better ameliorating) the mechanical properties of cotton.

To this aim, in the present work cotton fabrics were sol–gel treated using different precursors based on silicon, titanium, zirconium and aluminium, in order to investigate the thermal and fire stability, as well as the mechanical behaviour and abrasion resistance of the obtained materials. The morphology of the synthesized inorganic phases on cotton were evaluated by electron microscopy coupled to elemental analysis and results were directly correlated with the final resulting properties of cotton in terms of thermo-oxidative stability (thermogravimetric analysis in air), flammability (limiting oxygen index and vertical flame tests) and combustion behaviour (cone calorimetry). The mechanical properties (tensile strength and abrasion resistance) were investigated, as well.

2. Experimental

2.1. Materials

Cotton fabrics (CO, purchased from FratelliBallesio, Torino, Italy) with a density of 200 g/m^2 were used as received. Tetraethylorthosilicate, tetraethylorthotitanate, tetraethylorthozirconate and aluminium isopropylate, water, ethanol, propanol, acetic acid and dibutyltindiacetate (all reagent grades) were purchased from Sigma–Aldrich and used without any further purification.

2.2. Sol–gel treatments performed on cotton

Different inorganic coatings were synthesized on the cotton fabrics through sol–gel processes.

First of all, pure silica phases were obtained from a mixture containing tetraethylorthosilicate, distilled water (precursor:water molar ratio = 1:1), ethanol and dibutyltindiacetate (0.9 wt.%), that was stirred at room temperature for 10 min; the cotton fabrics were impregnated in the sol solution for 10 min and subsequently thermally treated at 80 °C for 15 h using a gravity convection oven. Finally, the fabrics were washed in distilled water at 60 °C for 1 h in order to eliminate the unreacted precursor.

Alumina sols were prepared according to Yoldas' method (Wong & Aziz, 2007). The appropriate amount of aluminium isopropylate was added to the deionized water and stirred 1 h at 80 °C. Then 1 M acetic acid solution was added to the mixture as a catalyst, setting the molar ratio of aluminium isopropylate:water:acetic acid at 1:100:0.7. The prepared solution was subsequently heated up to 90 °C and kept under reflux condition for 24 h until a fully transparent sol was obtained.

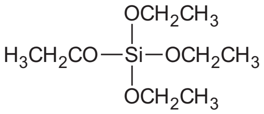
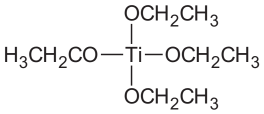
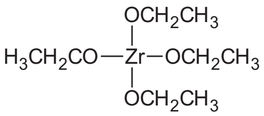
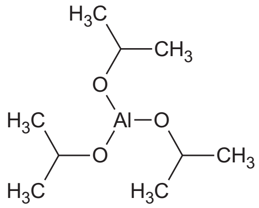
Titania sols were prepared starting from a mixture containing tetraethylorthotitanate, acetic acid and water (molar ratio 1:10:100). Thus, 60 ml of water were dropwise added to the mixture containing tetraethylorthotitanate and acetic acid with vigorous stirring for 2 h to get a clear transparent sol.

Finally, zirconia sols were obtained from tetraethylorthozirconate, which was added to a propanol and acetic acid solution and then mixed to another solution containing water and propanol under stirring for 2 h. The tetraethylorthozirconate:propanol:acetic acid:water molar ratio was 1:40:0.2:2.

The structures of the different metal alkoxides are schematized in Table 1.

In order to allow the formation of the inorganic coating, cotton fabrics were then immersed for 10 min in each solution, initially heated for 30 min at 100 °C and subsequently for 15 min at 120 °C.

Table 1
Structure of the used metal alkoxides.

Metal alkoxide	Structure
Tetraethylorthosilicate	 $H_3CH_2CO{-}\overset{OCH_2CH_3}{\underset{OCH_2CH_3}{Si}}{-}OCH_2CH_3$
Tetraethylorthotitanate	 $H_3CH_2CO{-}\overset{OCH_2CH_3}{\underset{OCH_2CH_3}{Ti}}{-}OCH_2CH_3$
Tetraethylorthozirconate	 $H_3CH_2CO{-}\overset{OCH_2CH_3}{\underset{OCH_2CH_3}{Zr}}{-}OCH_2CH_3$
Aluminium isopropylate	

Hereafter, each sample will be identified as *X*CO, where *X* is the metal of the employed alkoxide precursor; as an example, SiCO means cotton fabric treated with the silica sol.

2.3. Characterization techniques

The amounts of metal alkoxide phases 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 ($\pm 10^{-4}$ g). The upload, collected in Table 2, was calculated according to the following formula:

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

SEM images of the treated samples were obtained by a LEO-1450VP Scanning Electron Microscope (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. Cotton fabrics were cut into small pieces (0.5 mm × 0.5 mm) and fixed on a standard SEM sample holder by double-coated carbon conductive tab and then gold-metallized.

The thermal stability of the fabrics was evaluated by thermogravimetric (TG) analyses using a Pyris1TGAQ500 analyzer. The measurements were performed placing the samples in open alumina pans (ca. 10 mg) in air atmosphere (60 ml/min) from 50 to 800 °C with a heating rate of 10 °C/min. Further tests were performed by treating the fabrics in a muffle at 1100 °C for 1 h.

In order to determine the water content of neat and treated cotton fabrics, that can significantly influence the combustion behaviour of the materials, a Karl-Fisher titrator (Mettler Toledo, model V20) was used: small pieces (ca. 1 g) were heated up to 100 °C and the water content was measured by using a mixture of methanol, potassium metabisulphite and I_2 as titration system.

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

Table 2
TGA data in air.

Sample	A^a [%]	$T_{onset5\%}$ [°C]	$T_{max1}{}^b$ [°C]	$T_{max2}{}^b$ [°C]	Residue at 360 °C [%]	Residue at 500 °C [%]	Residue at 750 °C [%]	Residue at 1100 °C^c [%]
CO	–	316	347	485	20	2	0	0
SiCO	21	315	346	507	26	10	10	5
TiCO	22	293	326	445	32	11	9	4
ZrCO	22	284	340	498	31	11	7	4
AlCO	22	296	339	511	23	11	9	4

[a] Weight difference of cotton fabrics before and after impregnation/thermal treatment.
[b] From derivative curves.
[c] Residue after thermal treatment at 1100 °C in muffle.

The flammability test in a vertical configuration was carried out by applying once a propane flame for 5 s at the bottom of a fabric specimen (100 mm × 20 mm). 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 the ISO 15025 standard, commonly employed for the protective garments, with the exception that the specimen size adopted in the standard is larger (200 mm × 16 mm vs. 100 mm × 20 mm). In addition, the limiting oxygen index (LOI) tests were performed by a FIRE oxygen index apparatus according to the ISO 4589 standard.

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 conducted under an irradiative heat flow of 35 kW/m^2 in a horizontal configuration, following the procedure described elsewhere (Tata et al., 2011). Such parameters as Time To Ignition (TTI, s), Total Heat Release (THR, kW/m^2), Heat Release Rate (HRR, kW/m^2), peak (PHRR, kW/m^2) were measured and the Fire Performance Index (FPI, s m^2/kW) calculated as TTI to PHRR ratio. The higher the FPI, the better is the flame retardancy performance (Schartel, Bartholmai, & Knoll, 2006). Total Smoke Release (TSR, m^2/m^2) and Specific Extinction Area (SEA, m^2/Kg), were evaluated, as well. The experiments were repeated four times for each material investigated to ensure reproducible and significant data; the experimental error was within 2%.

Prior to flammability and combustion tests, all the specimens were conditioned at 23 ± 1 °C, for 24 h at 50% R.H in a climatic chamber.

The mechanical properties of pure and treated cotton fabrics were carried out on a Zwick Z100 apparatus in tensile configuration. The samples (350 mm × 50 mm) were prepared following the ISO 13934 standard: the distance between grips was 200 mm and the nominal strain rate was set at 10 mm/min. Five specimens of each formulation were tested; the experimental error was within 5%.

Finally, in order to assess the abrasion resistance of pure and treated fabrics, the samples were tested according to ISO 12947 standard (Martindale method).

3. Results and discussion

3.1. Thermal stability in air

Thermogravimetric curves of the samples in air are plotted in Fig. 1. For the untreated cellulosic fibres, three steps are visible as previously reported (Price et al., 1997): the first (at 347 °C, Table 2) involves two competitive pathways, which yield aliphatic char and volatile products; the second step, at 485 °C, corresponds to the conversion of aliphatic char into aromatic, producing carbon mono and dioxide due to the simultaneous carbonization. During the third and last decomposition step at ca. 800 °C, the char is oxidized.

We have already demonstrated that silica phases significantly change the thermal stability of cotton in air (Alongi, Ciobanu, Carosio, et al., 2011; Alongi et al., 2011a, 2011b, 2011c, in press). Indeed, silica acts as a physical barrier (*thermal insulator*), being able to protect cotton from heat and oxygen transfer and favouring the formation of a carbonaceous residue (10 vs. 0% for SiCO and CO at 750 °C, respectively, Table 2).

This finding was further confirmed by testing the same formulations at 1100 °C for 1 h in a muffle (last column of Table 2 and Fig. 2): indeed, unlike the sol–gel treated samples, after such thermal treatment, cotton was almost completely degraded and consumed.

Unlike silica, the other oxides (TiO_2, ZrO_2, Al_2O_3) change the degradation mechanism and kinetics of cellulose in terms of a significant reduction of the onset temperature ($T_{onset5\%}$: 293, 284 and 296, respectively, vs. 316 °C for pure cotton) and of the first decomposition step (T_{max1}), as observed in Fig. 1 and Table 2. Indeed, it is well described in the literature that metal ions can influence the thermal oxidative degradation of cotton cellulose since these species are able to catalyse the reaction of cellulose degradation/dehydration, favouring the formation of high amount of char. Generally, this effect is observed either when the metal ions are singularly used or in combination with phosphorus-based flame retardants (Tian, Xie, Guo, & Xu, 2003). As an example, Camino et al. (Soares, Camino, & Levchik, 1998) found that such organometallic additives as Zn-ethylhexanoate, K-ethylhexanoate and Co-ethylhexanoate, strongly modified the decomposition process of cellulose, enhancing the char and reducing tar formation. Furthermore, it was observed that Zn^{2+} and Co^{2+} are able to increase the formation of aromatic char, whereas K^+ ions provide aliphatic char. The action mechanism of metal ions changes when they are combined with phosphorus-based species, since they are able to increase their thermal stability. Indeed, the volatility of the phosphorus oxides formed during the pyrolysis is reduced and thus these species are still available to phosphorylate the cellulose and induce the char formation.

In particular, Horrocks and coworkers (Davies, Horrocks, & Alderson, 2005) have demonstrated that Mn^{2+} and Zn^{2+} shift the

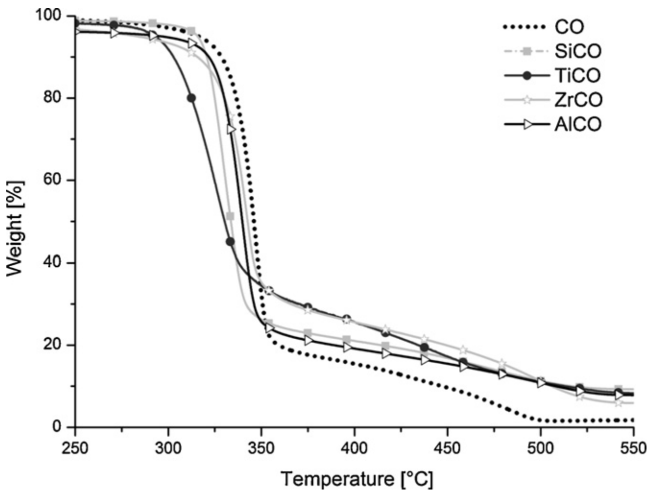


Fig. 1. TG curves of pure and sol–gel treated cotton fabrics in air.

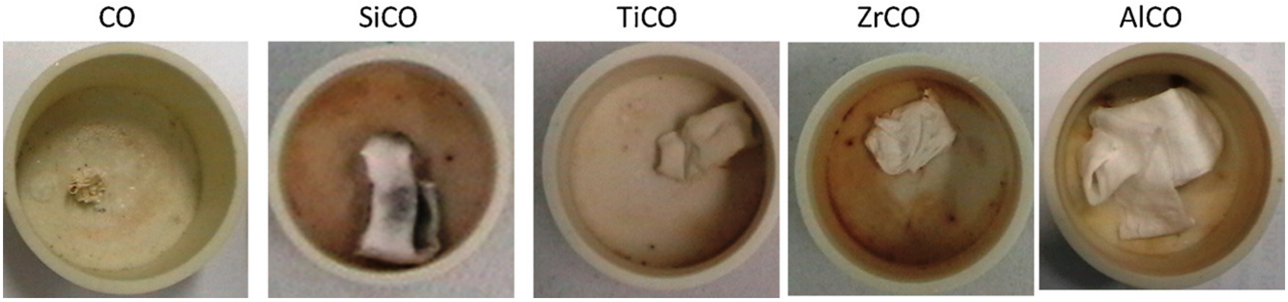


Fig. 2. Residues of pure and sol–gel treated cotton fabrics (samples having the same initial weight) after thermal treatment in muffle.

thermal degradation of ammonium polyphosphate toward lower temperatures, so that flame retardancy is induced at lower temperatures. Similar results were observed also employing other transition metal ions, such as Cu(II), Zn(II), Fe(II), Co(II), Cr(III), Ce(IV), La(III), Y(III) and Ho(III) or Mn(II), Pb(II), Bi(III) in combination with cellulose ammonium phosphate (Dahiya & Kumar, 2009; Tian, Guo, Zhang, Xu, & Shi, 1995; Tian et al., 2003). Indeed, Tian et al. (1995, 2003) observed that the temperature of cellulose decomposition was lowered in the presence of metal complexes of cellulose ammonium phosphate with respect to samples untreated by metal ions; furthermore, the values of char yield were greater for samples treated with Mn^{2+}, Pb^{2+}, Bi^{3+} (Tian et al., 2003) and Ho^{3+} and Ce^{3+} (Tian et al., 1995) than those untreated.

In the present work, all the formed oxides turn out to favour the formation of a higher char amount with respect to pure cotton, as indicated by the residues at 360 and 500 °C (Table 2). More specifically, Ti and Zr induce the formation of higher char amounts in comparison with Si and Al. On the basis of the previous studies published in the literature, it is possible to hypothesize that Ti and Zr ions catalyse the cellulose degradation more rapidly than Si and Al, anticipating the dehydration (as observable in the $T_{\text{onset5\%}}$)but, at the same time, favouring the char formation.

The high thermal stability in air of such treated fabrics is very useful to enhance their fire stability, as discussed in the next section.

3.2. Flammability

In order to identify the burning characteristics of the specimens, flammability tests were performed; the obtained results are collected in Table 3. In a previous work, we demonstrated that the silica coatings obtained by sol–gel processes are able to modify the cotton flammability in vertical configuration by i) decreasing its ignitability when cotton is exposed to a flame spread, ii) decreasing its burning kinetics and iii) increasing the total burning time (Alongi et al., 2011b). Thus, all the inorganic coatings are able to protect the cotton fabric against a direct propane flame. Indeed, the registered total burning time is increased, the burning rate is remarkably lowered and the final residue at the end of the test is higher than that of pure cotton (10% vs. 30, 31, 21 and 32% for SiCO, TiCO, ZrCO and AlCO, respectively).

Furthermore, comparing the performances of all the treated samples, it is possible to conclude that all the inorganic coatings are efficient flame retardants for cotton and that zirconia is less efficient than titania, silica and alumina as far as the final residue is concerned. These data are confirmed by the slight increase of LOI values for the treated fabrics, collected in Table 3.

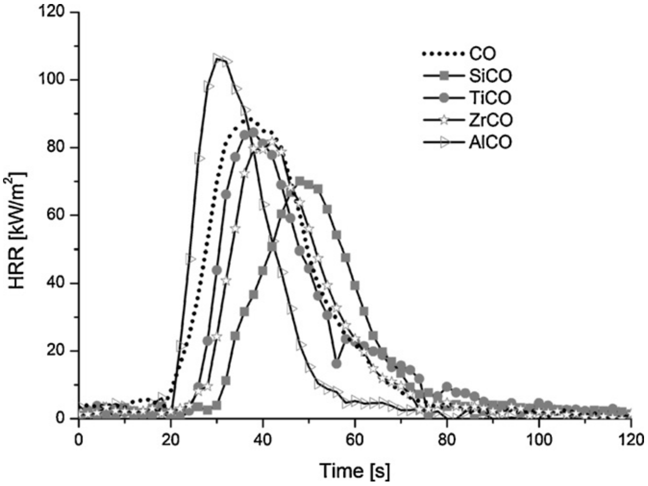


Fig. 3. HRR curves of pure and sol–gel treated cotton fabrics.

On the basis of these results, it is possible to establish a protective ranking exerted by the alkoxide coatings on cotton, starting from the most to the less efficient:

$$TiO_2 > SiO_2 > Al_2O_3 > ZrO_2$$

Correlating the flammability of these fabrics with their thermal properties, it is possible to observe that Ti ions, showing a higher efficiency in the dehydration of the cotton cellulose than Si, Al and Zr, turn out to be the best flame retardant among those under study. Although Zr ions behave like Ti during the thermal degradation of cotton in air, they have the worst performances in terms of flame retardancy probably because of the distribution level on the fibres, as will be discussed in the next section.

3.3. Combustion behaviour

The combustion data of pure and sol–gel treated cotton fabrics investigated by cone calorimeter are collected in Table 4; Fig. 3 plots

Table 3
Flammability data.

Sample	Total burning time [s]	Total burning rate [mm/s]	Residue [%]	LOI [%]
CO	20	20	10	19
SiCO	25	11	30	22
TiCO	29	9	31	22
ZrCO	24	12	21	21
AlCO	23	12	32	22

Table 4
Combustion data by cone calorimetry.

Sample	TTI [s]	THR [MJ/m^2]	PHRR [kW/m^2]	FPI [$s\cdot m^2$/kW]	TSR [m^2/m^2]	SEA [m^2/kg]	Water content [ppm][a]
CO	18	2.8	88	0.20	47.6	40.5	46,000
SiCO	28	2.0	70	0.40	11.3	15.2	71,000
TiCO	22	2.3	84	0.26	10.9	18.8	68,000
ZrCO	22	2.7	82	0.27	23.3	6.3	59,000
AlCO	20	1.9	106	0.19	22.0	13.0	57,000

[a] By Karl–Fisher titration.

the combustion kinetics of each sample in terms of HRR curves vs. time.

As already described in previous works (Alongi, Ciobanu, Carosio, et al., 2011; Alongi et al., 2011a, 2011b, 2011c, in press), silica is an efficient finishing flame retardant for cotton. Indeed, comparing the cotton to SiCO, TiCO, ZrCO, AlCO, it is clear that the presence of the inorganic coating onto the textile surface significantly modifies the combustion behaviour of cotton (Fig. 4). In general, a strong reduction of THR and PHRR is registered for all the systems (70, 84, 82 and 106 vs. 88 kW/m^2 for SiCO, TiCO, ZrCO, AlCO and CO, respectively, Table 4). Furthermore, such oxides are able to delay the sample ignition, increasing the TTI and consequently the FPI values (Table 4, Figs. 3 and 4). This effect is probably due to the water content entrapped within the coating, as determined by Karl–Fisher titration (Table 4). Unlike pure cotton, all the sol–gel treated fabrics show high water contents. During the initial degradation of cotton immediately before the combustion, water plays an important role because it is capable to postpone the ignition of the cellulose diluting the volatile products derived from its degradation: therefore, it is reasonable to hypothesize that the higher the water content, the higher is TTI (28, 22, 22 and 20 vs. 18 s for SiCO, TiCO, ZrCO, AlCO and CO, respectively). The relationship between TTI and water content is well depicted in Fig. 5a.

Furthermore, the observed TSR decrease (Fig. 4), can be also correlated with the water content. Indeed, SiCO and TiCO samples, having the highest water content (71,000 and 68,000 vs. 46,000 ppm) show the smallest TSR values (11.3 and 10.9 vs. 47.6 m^2/m^2) and consequently a reduced production of smokes. Analogously, the optical density of the smokes (SEA values) decreases by increasing the water content, as observed in Fig. 5b and Table 4. It is worth to note that such smoke reduction is very beneficial for exploiting the sol–gel treatment as an industrial finishing.

Finally, it is interesting to observe that the structure of final residue at the end of the combustion depends on the type of sol–gel treatment, as shown in Fig. 6. Silica and alumina are able to induce the formation of a thick, compact and dense residue, while titania and zirconia give a thin transparent film. In any case, the alkoxide phases allow to keep the original fabric structure thanks to the enhanced residue formation.

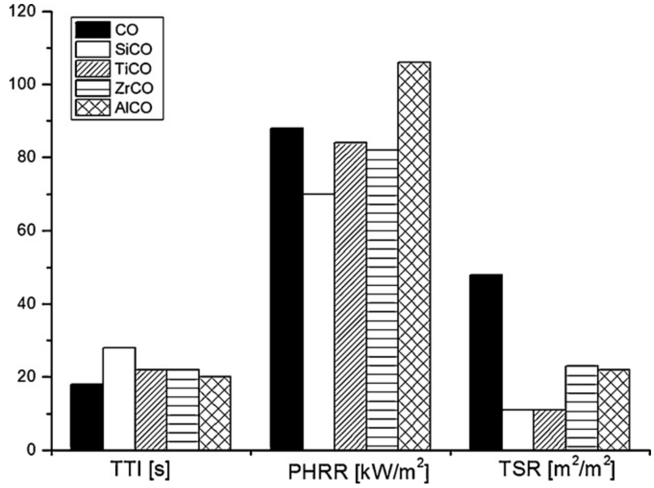


Fig. 4. TTI, PHRR and TSR values of neat and sol–gel treated cotton fabrics.

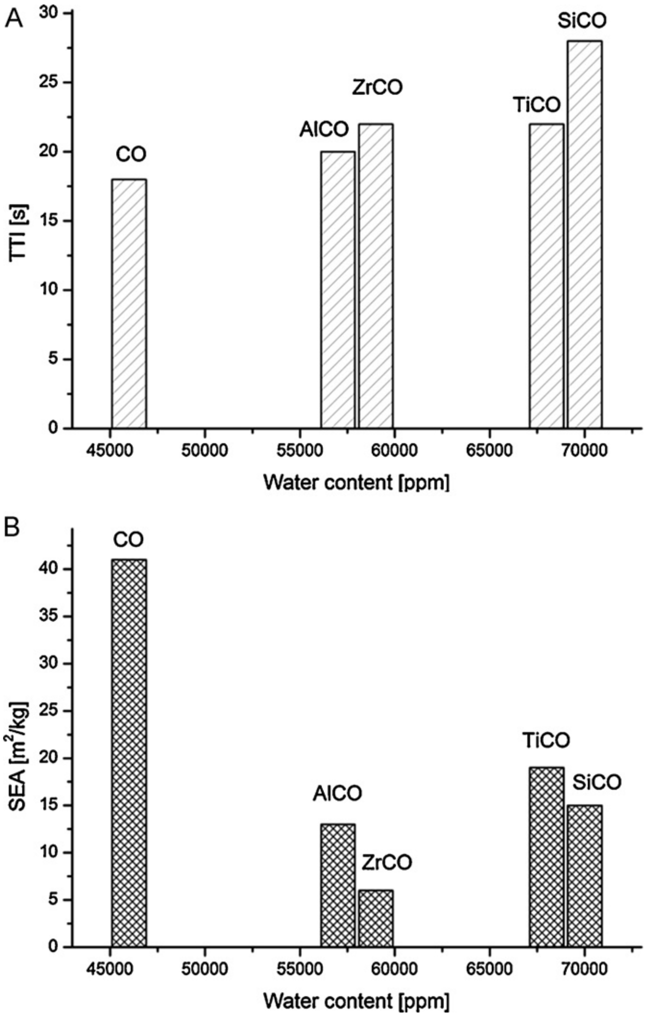


Fig. 5. TTI(a) and SEA(b) as functions of water amount for the different alkoxide coatings.

3.4. Morphology of the treated fabrics

Some typical SEM micrographs of the sol–gel treated cotton fabrics are reported in Fig. 7. In general, a homogeneous and compact film located at the fibre interstices (warp and weft) and partially covering their walls was observed for all the systems investigated; furthermore, few cracks are visible in SiCO and TiCO samples. The homogeneity of distribution of the inorganic coatings depends on the metal alkoxide precursor employed in the sol–gel process, as

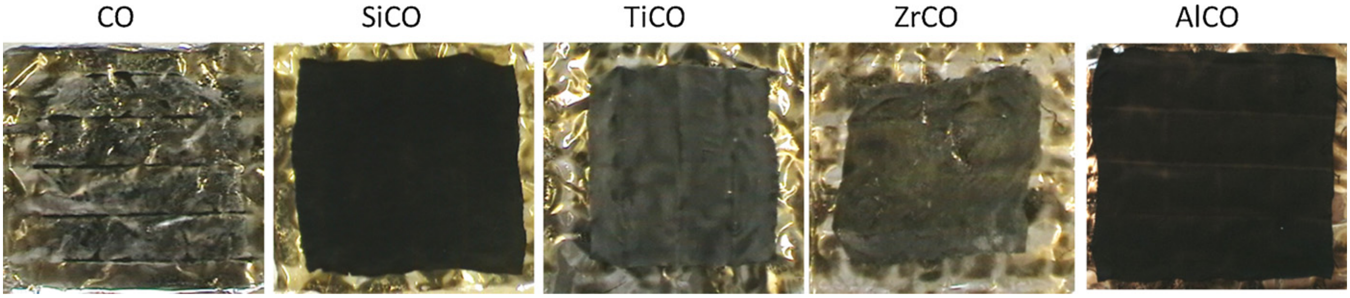


Fig. 6. Final residues of pure and sol–gel treated cotton fabrics after cone calorimetry tests.

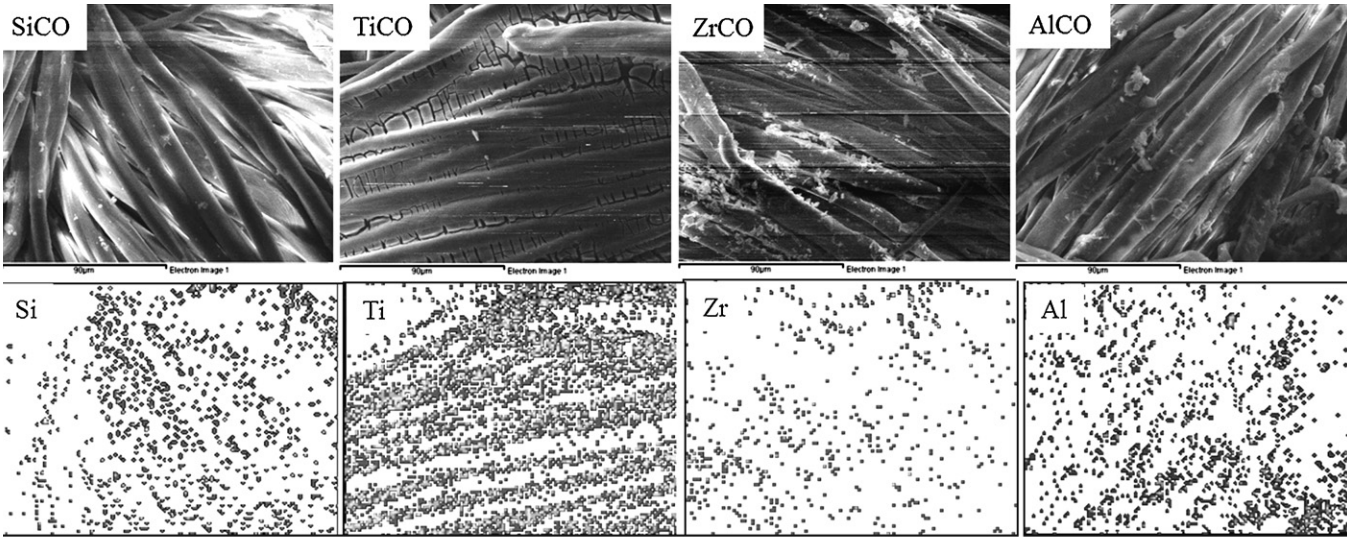


Fig. 7. SEM micrographs of sol–gel treated cotton fabrics and corresponding element maps.

pointed out by the elemental maps (Fig. 7). In particular, the best performances of titania with respect to the other inorganic coatings could be also ascribed to the very high level of homogeneity of Ti distribution. On the contrary, the Zr distribution appears to be less homogeneous and dense if compared with the other metals.

3.5. Mechanical properties and abrasion resistance

Usually, most of the chemical finishes applied to fabrics can promote undesirable changes in their mechanical properties in terms of resistance, smoothness and texture, due to the thickness and rigidity of the applied coating. In the presence of an applied force, if the coating is rigid, the fabric threads break one after the other and a low tear strength is registered. For this reason, in order to investigate the effect of sol–gel treatments on the mechanical strength of the fabrics, tensile and abrasion tests were conducted.

Table 5 summarises the collected data: after the sol–gel treatment, the maximum force slightly increases (1175, 1150 and 1100 vs. 1025 N for SiCO, TiCO, AlCO and CO, respectively) with the exception of ZrCO, which shows a slight decrease (975 N) with respect to pure cotton. In addition, the maximum deformation achieved by the sol–gel treated specimens is substantially unchanged. Therefore, these mechanical data indicate that the effect of the sol–gel treatment on cotton mechanical behaviour is almost negligible.

Fig. 8 plots the influence of the different alkoxide coatings on cotton abrasion resistance, measured by Martindale method. Pure cotton resists up to 2100 abrasion cycles, that correspond to the

Table 5
Tensile data.

Sample	Max strain [%]	Max force [N]
CO	22 ± 1.2	1025 ± 48
SiCO	21 ± 0.8	1175 ± 63
TiCO	21 ± 0.8	1150 ± 55
ZrCO	21 ± 1.0	975 ± 40
AlCO	20 ± 0.7	1100 ± 52

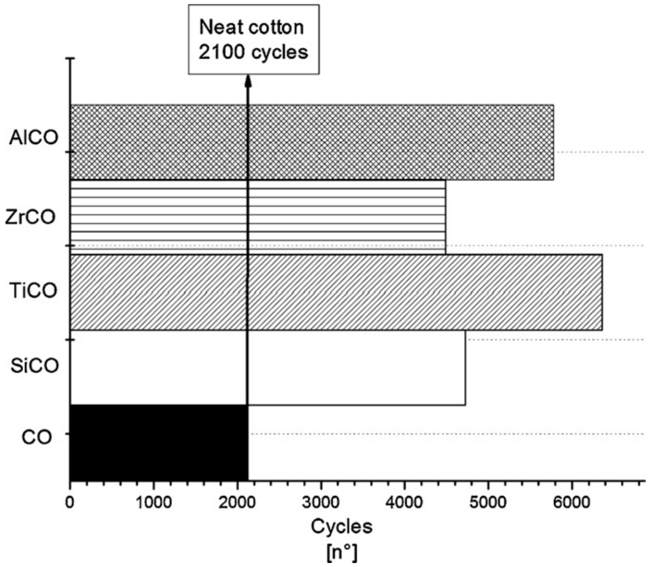


Fig. 8. Abrasion resistance of pure and sol–gel treated cotton fabrics.

end-point of the line since when a damage (e.g. a hole) appears on the sample surface. When cotton is sol–gel treated, the number of abrasion cycles necessary for the damage appearance is significantly increased and extended up to three times for TiCO and AlCO samples. These results clearly show that the inorganic coatings can strongly improve the abrasion resistance of the fabric. Furthermore, these tests indicate that the performance of zirconia is very low in comparison with the other metal oxides, probably because zirconia is not so well distributed as pointed out by electron microscopy (Fig. 7).

In conclusion, while the proposed sol–gel derived systems as flame retardant finishes do not cause mechanical undesirable changes with respect to untreated cotton, at the same time, the alkoxide coatings are able to strongly improve the abrasion resistance of the fabric.

4. Conclusions

Cotton fabrics were sol–gel treated exploiting the availability of different alkoxide precursors (tetraethylortho-silicate, -titanate, -zirconate and aluminium isopropylate). The fire performances of the treated fabrics, as well as the mechanical behaviour and abrasion resistance were evaluated. The coatings turned out to be responsible of an overall enhancement of the thermal and fire stability of the treated fabrics, which was ascribed to the morphology of the inorganic coatings on the fabric surface and to the water content in the treated textiles. At the same time, the effect of the sol–gel treatments on the mechanical behaviour of cotton was almost negligible, while a significant increase of the abrasion resistance was achieved.

These features may suggest that the sol–gel deposition of an essentially inorganic species could further add flame resistance at least to a cotton fabric possessing an already underlying level of flame retardant character.

References

Abidi, N., Hequet, E., Tarimala, S. & Dai, L. L. (2007). Cotton fabric surface modification for improved UV radiation protection using sol–gel process. *Journal of Applied Polymer Science*, *104*, 111–117.

Alongi, J., Ciobanu, M. & Malucelli, G. (2011a). Cotton fabrics treated with hybrid organic–inorganic coatings obtained through dual-cure processes. *Cellulose*, *18*, 1335–1338.

Alongi, J., Ciobanu, M. & Malucelli, G. (2011b). Sol–gel treatments for enhancing fire stability of cotton fabrics: optimization of the process and evaluation of durability. *Cellulose*, *18*, 167–177.

Alongi, J., Ciobanu, M. & Malucelli, G. (2011c). Novel flame retardant finishing systems for cotton fabrics based on phosphorus-containing compounds and silica derived from sol–gel processes. *Carbohydrate Polymers*, *85*, 599–608.

Alongi, J., Ciobanu, M., & Malucelli, G. (in press). Sol–gel treatments on cotton fabrics for improving thermal and flame stability: effect of the structure of the alkoxysilane precursor, *Carbohydrate Polymers*.

Alongi, J., Ciobanu, M., Carosio, F., Tata, J. & Malucelli, G. (2011). Thermal stability and flame retardancy of polyester, cotton and relative blend textile fabrics treated by sol–gel process. *Journal of Applied Polymer Science*, *119*, 1961–1969.

Burniston, N., Bygott, C. & Stratton, J. (2004). Nano technology meets titanium dioxide. *Surface Coatings International Part A*, *10*, 179–814.

Cireli, A., Onar, N., Ebeouglugil, M. F., Kayatekin, I., Kutlu, B., Culha, O. & Celik, E. (2007). Development of flame retardancy properties of new halogen-free phosphorus doped SiO_2 thin films on fabrics. *Journal of Applied Polymer Science*, *105*, 3747–3756.

Dahiya, J. B. & Kumar, K. (2009). Flame retardant study of cotton coated with intumescents: Kinetics and effect of metal ions. *Journal of Scientific & Industrial Research*, *68*, 548–554.

Daoud, W. A. & Xin, J. H. (2004). Nucleation and growth of anatase crystallites on cotton fabrics at low temperatures. *Journal of the American Ceramic Society*, *87*, 953–955.

Davies, P. J., Horrocks, A. R. & Alderson, A. (2005). The sensitisation of thermal decomposition of ammonium polyphosphate by selected metal ions and their potential for improved cotton fabric flame retardancy. *Polymer Degradation and Stability*, *88*, 114–122.

Dong, W. G. & Huang, G. (2002). Research on properties of nano polypropylene/TiO_2 composite fiber. *Journal of Textile Research*, *23*, 22–23.

Kathiervelu, S. S. (2003). Applications of nanotechnology in fibre finishing. *Synthetic Fibres*, *32*, 20–22.

Lecoeur, E., Vroman, I., Bourbigot, S., Lam, T. M. & Delobel, R. (2001). Flame retardant formulations for cotton. *Polymer Degradation and Stability*, *74*, 487–492.

Mahltig, B. & Fischer, A. (2010). Inorganic/organic polymer coatings for textiles to realize water repellent and antimicrobial properties—A study with respect to textile comfort. *Journal of Polymer Science: Part B Polymer Physics*, *48*, 1562–1568.

Moafi, H. F., Shojaie, A. F. & Zanjanchi, M. A. (2010). The comparison of photocatalytic activity of synthesized TiO_2 and ZrO_2 nanosize onto wool fibers. *Applied Surface Science*, *256*, 4310–4316.

Moafi, H. F., Shojaie, A. F. & Zanjanchi, M. A. (2011a). Flame-retardancy and photocatalytic properties of cellulosic fabric coated by nano-sized titanium dioxide. *Journal of Thermal Analysis and Calorimetry*, *104*, 717–724.

Moafi, H. F., Shojaie, A. F. & Zanjanchi, M. A. (2011b). Titania and titania nanocomposites on cellulosic fibers: Synthesis, characterization and comparative study of photocatalytic activity. *Chemical Engineering Journal*, *166*, 413–419.

Nie, Y. B., Yu, J. X., Yu, A. P., Chen, X. H. & Gu, H. C. (2002). Preparation and application of novel fabric finishing agent containing nano ATO. *Journal of Functional Polymers*, *15*, 43–47.

Price, D., Horrocks, A. R., Akalin, M. & Faroq, A. A. (1997). Influence of flame retardants on the mechanism of pyrolysis of cotton (cellulose) fabrics in air. *Journal of Analytical and Applied Pyrolysis*, *40/41*, 511–524.

Rosace, G., Canton, R. & Colleoni, C. (2010). Plasma enhanced CVD of $SiO_xC_yH_z$ thin film on different textile fabrics: Influence of exposure time on the abrasion resistance and mechanical properties. *Applied Surface Science*, *256*, 2509–2516.

Russell, E. (2002). Nanotechnologies and the shrinking world of textiles. *Textile Horizons*, *9/10*, 7–9.

Sakka, S. (2003). *Sol–gel science and technology. Topics and fundamental research and applications. Vols. 1–4* Norewll, Massachussetts: Kluwer Academic Publishers.

Schartel, B., Bartholmai, M. & Knoll, U. (2006). Some comments on the main fire retardancy mechanisms in polymer nanocomposites. *Polymers for Advanced Technologies*, *17*, 772–776.

Soares, S., Camino, G. & Levchik, S. (1998). Effect of metal carboxylates on the thermal decomposition of cellulose. *Polymer Degradation and Stability*, *62*, 25–31.

Tata, J., Alongi, J., Carosio, F. & Frache, A. (2011). Optimization of the procedure to burn textile fabrics by cone calorimeter: part I. Combustion behavior of polyester. *Fire and Materials*, *35*, 397–409.

Tian, C. M., Guo, H. Z., Zhang, H. Y., Xu, J. Z. & Shi, J. R. (1995). Study on the thermal degradation of cotton cellulose ammonium phosphate and its metal complexes. *Thermochimica Acta*, *253*, 243–251.

Tian, C. M., Xie, J. X., Guo, H. Z. & Xu, J. Z. (2003). Effect of metal ions on thermal oxidative degradation of cotton cellulose ammonium phosphate. *Journal of Thermal Analysis and Calorimetry*, *73*, 827–834.

Wang, W. & Chen, S. L. (2005). Application of nanosol on the antistatic property of polyester. *Melliand International*, *11*, 56–59.

Wong, F. L. & Aziz, A. A. (2007). Development of crack-free alumina sol–gel/poly(vinyl alcohol) membranes for glucose oxidase immobilization. *Asian Journal of Chemical Engineering*, *7*, 61–67.

Xiao, X., Chen, F., Wei, Q. & Wu, N. (2009). Surface modification of polyester nonwoven fabrics by Al_2O_3 sol–gel coating. *Journal of Coatings Technology and Research*, *6*, 537–541.

Xin, J. H., Daoud, W. A. & Kong, Y. Y. (2004). A new approach to UV-blocking treatment for cotton fabrics. *Textile Research Journal*, *74*, 97–100.

Yang, H. Y., Zhu, S. K. & Pan, N. (2003). Studying the mechanisms of titanium dioxide as ultraviolet-blocking additive for films and fabrics by an improved scheme. *Journal of Applied Polymer Science*, *92*, 3201–3210.