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# Thermal stability, flame retardancy and abrasion resistance of cotton and cotton–linen blends treated by sol–gel silica coatings containing alumina micro- or nano-particles

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ABSTRACT

Sol–gel processes have been carried out to deposit silica coatings "doped" with alumina micro- or nano-particles on cotton and cotton–linen fabrics in order to enhance their thermal stability, flame retardancy and mechanical properties (namely, abrasion resistance).

The joint effect between silica and alumina particles (regardless of their size) has proven to enhance the thermal stability in air, and consequently to affect the flame retardancy of the treated fabrics, as assessed by thermogravimetry, flammability and cone calorimetry tests. Furthermore, the presence of traces of alumina particles has turned out to be responsible of a remarkable increase of the abrasion resistance of the fabrics.



## 1. Introduction

In the last years, the interest for the sol–gel processes in the textile field has grown in a remarkable way. Indeed, the sol–gel approach has been recently used for introducing new functional properties, such as antimicrobial or UV radiation protection [1–6], dye fastness [7,8], anti-wrinkle finishing [9], super-hydrophobicity [10,11], and immobilization of biomolecules [12]. Despite the fact that this technique has been in use since the 1950s, its application for conferring flame retardancy to textiles is very recent and has only been documented in the last five years by a few research groups [13–17].

In particular, it has been clearly demonstrated that sol–gel derived hybrid architectures are capable to protect the polymer surface acting as thermal insulator, thus improving the flame retardancy of the treated substrates [17]. More specifically, referring to cellulosic substrates, these inorganic architectures, absorbing the heat from the surrounding area, are able to protect the polymer substrate, by creating a physical barrier to oxygen and heat transfer, hindering the formation of volatile species that fuel the further degradation and, at the same time, favouring the formation of a carbonaceous structure (*char*). As a matter of fact, such architectures operate only in the condensed phase during the combustion of a polymeric material and not in the vapour phase. To overcome this limitation, joint or synergistic effects achieved by combining the sol–gel oxidic phases with suitable species, active in the vapour phase, can be exploited [16,17]. In this scenario, we have already demonstrated that it is possible to enhance the flame retardant properties of cotton, by depositing other oxidic phases such as titania, zirconia or alumina, instead of silica, starting from different other alkoxide precursors than tetraethylortho-silicate (namely, tetraethylortho-titanate, -zirconate or aluminium isopropylate) [18]. These 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 of 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. More specifically, alumina- and titania-based coatings have shown very good results in terms of abrasion resistance, but worse performances of flame retardancy with respect to silica. For this reason, the aim of the present work is to investigate the possibility to reach an optimal formulation

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for conferring both these features to the fabrics, exploiting the characteristics of two different ceramics (i.e. silica and alumina). More specifically, silica coatings containing alumina micro- or nano-particles have been deposited on cotton fabrics in order to investigate their thermal stability, flame retardancy and abrasion resistance. These properties have been assessed by thermogravimetry in inert and oxidative atmospheres, flammability, combustion and abrasion resistance tests. Furthermore, the same coatings have been deposited on cotton–linen fabrics, as well, in order to assess whether these oxide phases are suitable for cellulosic substrates other than cotton.

## 2. Experimental part

### 2.1. Materials

Cotton fabrics (COT) with a density of 200 g/m$^2$ were purchased from Fratelli Ballesio (Torino, Italy) and used as received; 40:60 cotton–linen blends (COT/LI, 260 g/m$^2$, Fratelli Ballesio) were also employed as substrates for the sol–gel treatments. Tetramethylorthosilicate, ethanol, and dibutyltindiacetate (all reagent grades), as well as alumina micro- and nano-particles (325 and 50 nm, coded as AM and AN, respectively) were purchased from Sigma–Aldrich. 14.6 μS deionized water was supplied by a Millipore system (Billerica, MA, USA).

### 2.2. Sol–gel treatments performed on cotton

Pure silica phases were obtained from a mixture containing tetramethylorthosilicate, distilled water (precursor:water molar ratio = 1:1), ethanol and dibutyltindiacetate (0.9 wt.%), that was stirred at room temperature for 10 min; then, 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 particles have been added to the sol before the impregnation of the fabrics, at the maximum concentration allowed preventing any precipitation from the sol solution (namely, 1 and 0.5 g for AM and AN in 100 ml sol, respectively).

Hereafter, each sample will be identified as COT_X, where X indicates silica (S) or silica phases containing micro- or nano-alumina particles (SAM or SAN, respectively).

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

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

**Table 1**
Formulations under investigation.

| Code | $A$[a] [%] |
|---|---|
| COT_S | 20 |
| COT_SAM | 24 |
| COT_SAN | 24 |
| COT/LI_S | 25 |
| COT/LI_SAM | 29 |
| COT/LI_SAN | 30 |

[a] Final add-on after the sol–gel treatment.

### 2.3. Characterization techniques

XRD analyses were performed on 30 × 30 × 0.5 mm$^3$ samples with a Philips X'Pert-MPD diffractometer (Cu-K$_\alpha$ radiation, $k$ = 1.540562 Å; step size: 0.02°; step time: 2 s).

SEM images of the treated samples were obtained by a LEO-1450VP Scanning Electron Microscope (5 kV), equipped with an X-ray probe (INCA Energy Oxford, Cu-K$_\alpha$ X-ray source, $k$ = 1.540562 Å), which was used to perform elemental analysis. The fabrics were cut into small pieces (0.5 × 0.5 mm$^2$) 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 TA Q500 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 heating the fabrics in an F.A.V.S. muffle (ME320 model, Torino, Italy) at 1100 °C for 0.5 h.

The flammability of the prepared samples was measured using a vertical test, applying a methane flame for 5 s at the bottom of a fabric specimen (50 × 150 mm$^2$) and repeating the test 3 times for each formulation in order to obtain reproducible data; total burning time, total burning rate and final residue were measured. This test aims to mimic the procedure described in the ISO 15025 standard, commonly employed for protective garments, although the specimen size is different (200 × 16 mm$^2$ in ISO 15025).

The combustion behaviour of square fabric samples (100 × 100 × 0.5 mm$^3$) was investigated using cone calorimetry (Fire Testing Technology, FTT). The measurements were carried out under an irradiative heat flow of 35 kW/m$^2$ in horizontal configuration, following the procedure described elsewhere [19]. Time To Ignition (TTI, s), Total Heat Release (THR, kW/m$^2$), Heat Release Rate (HRR, kW/m$^2$), and peak (PHRR, kW/m$^2$) were measured. The experiments were repeated four times for each material investigated to ensure reproducible and significant data; the standard deviation ($\sigma$) was calculated, as well.

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.

In order to assess the abrasion resistance of untreated and sol–gel treated fabrics, the samples were tested according to the ISO 12947 standard (Martindale method).

## 3. Results and discussion

### 3.1. X-ray diffraction

X-ray diffraction has been employed in order to assess the crystallinity pattern of pure and sol–gel treated cotton fabrics. Indeed, cellulose of cotton fibres is highly crystalline and oriented: more specifically, the supramolecular structure of cellulosic fibres can be described by a two-phase model with regions of high orientation (crystalline form) and low orientation (amorphous form) [20]. According to the literature [21], in the XRD pattern of pure cotton (Fig. 1A), four main peaks ascribed to cellulose are present at ca. 15°, 17°, 22° and 34°, corresponding to the main planes of reflection (1 0 1), (1 0 $\bar{1}$), (0 0 2), and (0 4 0). The deposition of a coating consisting of pure silica induces a slight shift of these peaks towards lower angles and the appearance of two new peaks at 37° and 44° attributable to the silica. The XRD pattern of the samples treated with silica and alumina does not show significant changes, with the exception of the appearance of a less intense peak at 57° for COT_SAM and a slight broadening of the peak at 34° for COT_SAN, respectively, according to the XRD