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Sol-gel based coatings for the protection of cultural heritage textiles

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Abstract. In this paper, the procedure for the development of sol-gel silica coatings for the protection of cultural heritage textiles, using a multistep approach, is described. With this aim, Tetraethoxysilane precursor was used at two different concentrations to realize coatings onto textile samples, using Dibutyltindiacetate as polycondensation catalyst for sol-gel reactions. The relationship between the presence of the catalyst, the number of coating layers deposited on cotton fabrics, and the influence of such architecture on several properties of treated textiles, were investigated. In particular, the chemical structure of thin films and their morphology were studied by infrared spectroscopy and scanning electron microscopy, respectively. The thermo-oxidative properties and the abrasion resistance of sol-gel treated cotton fabrics were studied, as well as the durability of the coatings after different washing cycles. Both silica coatings provided high adhesion onto cotton textiles, while the higher silica concentration resulted in higher thermal stability and washing fastness of treated fabrics. An enhancement in the washing fastness and abrasion resistance for the two different concentrations of precursor in the presence of the catalyst was also observed. All experimental findings demonstrated the efficiency of sol-gel based materials specifically tailored to the protection and preservation of cultural heritage textiles.

1. Introduction

Ancient and archaeological textiles are a precious historical-artistic heritage, which must be protected against the deterioration with time induced by environmental agents, such as light, temperature and humidity changes, as well as atmospheric pollutants. Generally, the materials employed in the preservation or restoration of textiles with historical and artistic value, are commercial products, with properties not specifically developed for the conservation of natural polymers [1,2]. Graft copolymerization of vinyl monomers onto linen and cotton fabrics were successful investigated due to their consolidating and protective effects [3]. Recent scientific advances led to a wide array of new coatings based on nanostructured materials tailored for conservation and protection of the cultural heritage. Among them, many scientific reports are concerning the application of such materials, synthesized by the sol-gel method, in the conservation and consolidation of stones and glasses [4].

According to this technology, it is possible to realize advanced materials with a high degree of homogeneity at molecular level and unique physical-chemical properties. Based on subsequently hydrolysis and condensation reactions, this versatile and cheap synthetic strategy, performed at low temperature, conducts to inorganic or hybrid organic-inorganic networks by starting from metal alkoxide precursors [5,6]. The thin silica films can be applied as protective coatings on materials surface, among which textile fabrics: it has been found that the colloidal silica improves the mechanical properties of the substrate allowing good optical transparency, and provides further features such as hardness, anti-corrosion, wear resistance and so on [7,8]. Indeed, the hybrid organic-inorganic sol-gel coatings are able to improve or confer several fabric performances, such as flame retardancy [9-11], UV protection [12], water repellency [13,14], as well as antimicrobial [15,16], and halochromic properties [6,17-22], among many.

Tetraethoxysilane (TEOS) is a silica inorganic alkoxide widely employed in the sol-gel technique and several studies have been conducted to study the adhesion of silica coatings on the surface of different materials such as glasses, plastics, metals, and textiles [23,24]. The employment of catalysts, both acids or bases, strongly influences the gelation process of TEOS [25] and also leads to adverse effects mainly consisting of the potential aggressiveness for treated material. In this regard, recently, Dibutyltindilaurate (DBTL) and Dibutyltindiacetate (DBTA), usually employed for stone conservation applications, have been investigated as organic-tin catalysts for polycondensation of sol-gel reactions [26,27]. In this work, Tetraethoxysilane and Dibutyltindiacetate (the sol-gel precursor and polycondensation catalyst, respectively) were used at different concentrations to realize protective coatings onto cellulose-based textile samples. With this aim, a multilayer approach consisting of the deposition of 1-to-6 consecutive TEOS layers for each used concentration (0.03 M and 0.3 M), with and without the presence of DBTA as the last layer onto fabric samples, was developed to thoroughly study the properties that can be achieved on treated samples. The chemical composition, the thermo-oxidative properties, the morphology and the abrasion resistance of the treated cotton fabrics were deeply investigated as function of both TEOS concentration and numbers of layers applied onto cotton fabrics. Moreover, the durability of the coatings after 1 and 5 washing cycles was assessed. The final goal of this research is to demonstrate the potential use of the sol-gel technique in the effective protection of cellulose-based polymer used in cultural heritage textiles, opening up a large research landscape no entirely investigated.

2. Experimental part

2.1. Materials
Scoured and bleached cotton fabrics, with a mass per unit area of 200 g/m^2, were employed in this research as a reference of fabric samples used in the preservation or restoration of textiles for cultural heritage applications. Before experiments, fabric samples underwent a washing cycle in a non-ionic detergent (2%) at 40°C for 20 minutes. After rinsing with deionized water and drying, the fabrics were conditioned under standard atmospheric pressure at 65±4% relative humidity and 20±2°C for at least 24 hours. For all performed experiments, Tetraethylorthosilicate (TEOS, ≥ 98%), Dibutyltindiacetate (DBTA), hydrochloric acid (HCl) and ethanol were purchased from Sigma-Aldrich and used without further purification.

2.2. Synthesis of TEOS coatings and application onto cotton fabrics
A 0.3 M TEOS solution was obtained through the hydrolysis of TEOS in deionized water in the presence of ethanol (6 mL) and HCl (0.1 M, 4 mL) under vigorous stirring for 5 h at room temperature. Then, the same solution was diluted by 10 times with water to obtain a second 0.03 M TEOS solution. The DBTA (8% v/v, on TEOS amount) was used as an ethanol solution and applied on cotton fabrics as the last layer. Each TEOS solution (0.03 M and 0.3 M) was applied onto cotton fabrics by a two-roll laboratory padder with a wet pick-up of 70%. The treated samples (CO_t and CO_T, cotton fabric treated with 0.03 M TEOS and with 0.3 M TEOS solutions, respectively) were dried (90°C for 5 min), re-coated with the

same TEOS solution (to obtain CO_n, where "n" refers to 1, 3 and 6 layers), or treated with the catalyst solution (CO_nC), and finally cured (160°C for 5 min). The samples were conditioned under standard conditions for at least 24 h, before all the characterizations.

The following equation (1) was used to evaluate the total dry solid add-on (wt.%):

$$Add\text{-}on = \frac{W_T - W_{UT}}{W_{UT}} \cdot 100 \tag{1}$$

In Equation (1), W_{UT} and W_T are the dry weights of untreated and treated fabrics, respectively.

The washing fastness properties of the applied coatings onto cotton surfaces were also investigated. Treated fabrics were subjected to 1 and 5 laundering cycles according to the standard EN ISO 6330:2012, and the weight loss of silica coatings after washing cycles (WLW, wt.%) was calculated according to Equation (2):

$$WLW = \frac{Add\text{-}on_w}{Add\text{-}on_{uw}} \cdot 100 \tag{2}$$

where $Add\text{-}on_w$ and $Add\text{-}on_{uw}$ are the total dry solid add-on of washed and unwashed cotton samples, respectively. All samples were weighted three times using a Mettler balance ($\pm$ 10^{-4} g), and an average value was calculated with a standard deviation lower than $\pm 2\%$.

2.3. Characterization techniques

Both untreated and treated cotton fabrics were investigated through FTIR spectroscopy to assess the chemical composition of the applied silica layer. A Thermo Avatar 370 spectrometer, equipped with an attenuated total reflection (ATR) accessory and a diamond crystal as an internal reflectance element, was used for these characterizations. FTIR spectra of both untreated and treated cotton fabrics were recorded in the range from 4000 to 700 cm^{-1}, acquiring 32 scans with a resolution of 4 cm^{-1} and reported in terms of Absorbance after normalization at 1315 cm^{-1} (CH_2 wagging of cellulose).

Morphology of both untreated and treated cotton fabrics was investigated through Scanning Electron Microscopy (SEM) using a JEOL instrument (model JSM-6380LV) coupled with Energy Dispersive Spectrometer (EDS) and operating at 20 kV.

Thermo-oxidative properties of all samples were assessed through Thermogravimetric analysis (TGA). These characterizations were performed by a TA Instruments Model TGA Q500 operating under N_2 or air atmosphere in the range 30–600°C, with a heating rate of 10°C/min and 60 mL/min gas flow.

Treated cotton samples were tested according to DIN EN ISO 12947-3 (Martindale method) to assess their abrasion resistance. A pressure of abrasive heads of 9 kPa was used, and the weight loss (wt.%) of samples was calculated for four abrasion levels (namely 5,000; 10,000; 15,000; 20,000; corresponding to the number of rubs) according to Equation (3):

$$Weight\ loss = \frac{W_f - Wi}{W_i} \cdot 100 \tag{3}$$

where W_i and W_f are the weight of the sample before and after abrasion cycles, respectively. All samples were weighted five times using a Mettler balance ($\pm$ 10^{-4} g), and an average value was calculated with a standard deviation lower than $\pm 1\%$.

An Instron Tensile Tester model 4501 was used to investigate the tensile strength of treated samples following ASTM D5035 standard. Five specimens for warp and five for weft direction were tested. Pretension of 0.5 ± 0.1 cN tex^{-1} and a load cell of 1000 cN were used.

3. Results and discussion

3.1. Add-on of treated cotton fabrics and chemical composition of TEOS coatings

Treated cotton fabrics were studied by means of gravimetric tests as a function of different TEOS concentrations, numbers of applied layers and presence of the catalyst as last layer. Gravimetric analyses reveal the same add-on (wt.%) for CO_t independently from both the number of applied layers and presence of the catalyst (Figure 1). Contrary, the higher the number of TEOS layers onto cotton fabric

the higher the add-on (wt.%) of CO_T samples, with values up to 14.5 % (Figure 1) regardless the presence of the catalyst. This behavior is due to the interaction of the last TEOS coating with a previous one according to covalent bonds. The Si-OH of the silica layer onto cotton surfaces form an inorganic network highly interconnected with fibers by weak interactions whose strength influences the adhesion of the coating onto cotton fabrics. For the first silica layer, the adhesion of the coating is influenced by the diffusion of silica particles from the fabric surface into the fabric texture, while increasing the number of layers, the influence of cotton becomes less relevant and the linear increase in the add-on (wt.%) is due to covalent bonds established between two consecutive TEOS layers.
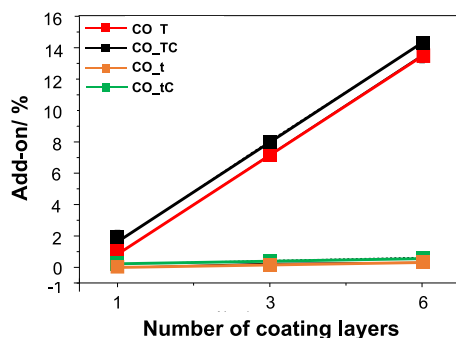

Figure 1. Add-on (wt.%) of cotton samples treated with 1, 3, and 6 layers of 0.03 M (CO_t) and 0.3 M TEOS solutions (CO_T), with and without the catalyst.

Both ATR-FTIR spectra of CO_t and CO_T are similar, and differences in the absorption intensity between untreated and treated cotton samples are more evident for CO_T samples because of the higher concentration of the deposited silica finishing. For this reason, only FTIR spectra of CO_T fabrics are reported in Figure 2. The characteristic absorption bands of cellulose in the range 3500 – 3000 cm^{-1} (O-H stretching), 2980 -2800 cm^{-1} (C-H stretching) and 1433 – 1428 cm^{-1} (C-H wagging) do not show significant changes in their intensity after the deposition of TEOS coatings [28]. FTIR peaks at 1202 cm^{-1}, 953 cm^{-1}, 796 cm^{-1} (Si-O stretching vibration, Si-OH stretching, and Si-O-Si symmetric stretching, respectively), confirm the presence of the TEOS layers onto the cotton surface [18,20]. By referring to the silica coatings, only the Si-O-Si asymmetric stretching peak (1018 cm^{-1}) [17,19] was not distinctly observed because of its overlapping by cellulose absorption bands in the range 1050 - 980 cm^{-1}. As shown by spectra in Figure 2, the presence of DBTA catalyst does not influence the FTIR profile of treated samples significantly.
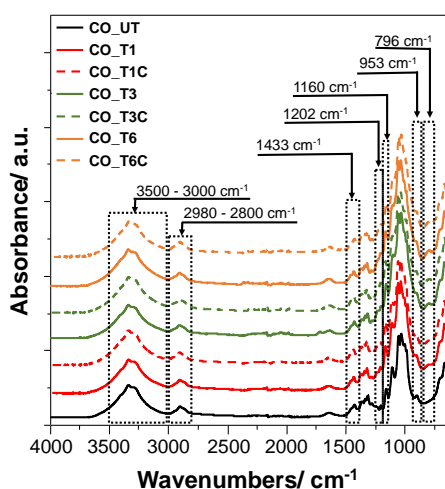

Figure 2. Comparison between ATR-FTIR spectra of CO_UT and CO_T from 1 to 6 silica layer application, with and without the catalyst (dashed and solid curves, respectively).

3.2. Washing fastness

The durability of the silica coatings onto cotton substrates was assessed in terms of washing fastness after 1 and 5 launder cycles as described in the experimental part and average WLW (wt.%) values for

both CO_t and CO_T samples are reported in Table 1. Results revealed weight losses ranging from less than 1 up to 3 % in the absence of the catalyst with lower values for CO_T compared to those of CO_t samples. The presence of the catalyst reduces the weight loss of all samples below 1% thus confirming that DBTA enhances the durability of the coating by creating a compact and more durable surface onto fibers and that the silica film is firmly attached to the cotton surfaces.
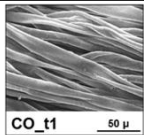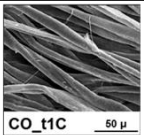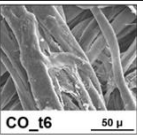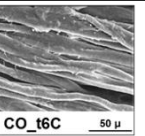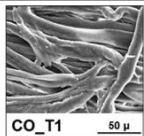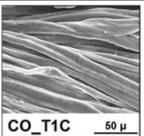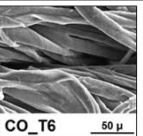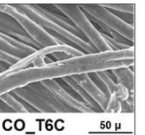
Table 1. Weight loss (WLW, wt.%) for CO_t and CO_T after 1 and 5 washing cycles (1w and 5w, respectively) at different number of layers (1 to 6) with and without the catalyst.

Sample	WLW (%)		Sample	WLW (%)	
	1w	5w		1w	5w
CO_t1	3.2	3.3	CO_T1	0.9	0.9
CO_t3	1.2	1.9	CO_T3	0.6	1.1
CO_t6	1.0	1.6	CO_T6	0.7	1.4
CO_t1C	0.6	0.6	CO_T1C	0.5	0.6
CO_t3C	0.3	0.6	CO_T3C	0.5	0.7
CO_t6C	0.4	0.5	CO_T6C	0.6	0.6

3.3. Morphological properties

The morphology of treated cotton samples and the influence of the multi-layer architecture on it were investigated through SEM characterizations, and images of both 1 and 6 layers CO_t and CO_T samples, with and without the catalyst, are reported in Table 2. Moreover, EDS analysis was performed on treated samples and results, in terms of Si and Sn amount (wt.%), are reported also in Table 2 and referred to the presence of silica coatings and the catalyst on fabrics, respectively. SEM images confirm that the thin TEOS layer is more detectable increasing the silica layers, while the presence of DBTA does not affect the morphology of treated cotton samples significantly. EDS analysis revealed the higher Si amount for CO_T with increasing TEOS layers, and the presence of Sn in the cotton samples treated with the catalyst.

Table 2. SEM images of 1 and 6 layers CO_t and CO_T, with and without catalyst, with the corresponding Si and Sn amount (wt.%) from EDS analysis.

Sample	CO_t1 50 μ	CO_t1C 50 μ	CO_t6 50 μ	CO_t6C 50 μ
Si [%]	1.9 ± 0.2	2.0 ± 0.2	5.2 ± 0.4	5.2 ± 0.5
Sn [%]	-	0.5 ± 0.1	-	0.9 ± 0.1
Sample	CO_T1 50 μ	CO_T1C 50 μ	CO_T6 50 μ	CO_T6C 50 μ
Si [%]	6.2 ± 0.6	5.2 ± 0.5	9.9 ± 0.9	8.2 ± 0.8
Sn [%]	-	1.0 ± 0.1	-	1.5 ± 0.1

3.4. Thermo-oxidative properties

In Table 3, the thermo-oxidative behavior of untreated and treated cotton fabrics with both employed TEOS concentrations are reported in terms of the temperature of the maximum weight loss (T_{dec}) and

char formation (char residue). As shown by data reported in Table 3, the main thermo-oxidative degradation of untreated cotton fabric occurs at 336°C, to then completely burn at 600°C, as shown by the negligible char residue. The decomposition temperatures of treated samples are lower than that of untreated cotton, except for CO_t samples in absence of DBTA. The char residue percentages of CO_T samples are higher compared to CO_t thus suggesting good thermal stability of 0.3 M TEOS coating on cotton. Moreover, an increase in the char residue was observed for CO_T samples with increasing the number of layers. The presence of the catalyst seems to do not affect the decomposition temperature of these samples, while it contributes to the reduction of the char residue. An opposite effect of DBTA was observed for cotton samples treated with the lower TEOS concentration: catalyst provided a decrease in the decomposition temperature and an increase in the char residue compared to cotton samples treated without catalyst. According to these results, CO_t revealed a similar thermal degradation of untreated cotton and lower char residue than that obtained from CO_T samples. These experimental data confirm the efficacy of the higher silica concentration for the improvement of thermo-oxidative performances of cotton fabrics.

Table 3. Decomposition temperatures ($T_{dec,}$ °C) and char residue (%) at 600°C of cotton samples in air.

Sample	T_{dec} (°C)	Char residue (%)	Sample	T_{dec} (°C)	Char residue (%)
CO_UT	336	< 0.5	CO_UT	336	< 0.5
CO_t1	336	0.3	CO_T1	332	3.1
CO_t3	336	1.0	CO_T3	320	12.0
CO_t6	336	0.9	CO_T6	315	24.8
CO_t1C	336	2.5	CO_T1C	329	2.6
CO_t3C	332	2.5	CO_T3C	320	9.2
CO_t6C	322	5.1	CO_T6C	322	13.9

3.5. Abrasion resistance and mechanical properties of treated cotton fabrics

Martindale tests caused the broken of cotton samples treated with 0.3 M TEOS concentration, and for this reason in Figure 3, only data of Martindale tests for CO_t are reported. As shown by the graph in Figure 3, the general trend of Martindale tests consists of the increase in the weight losses (wt.%) of both untreated and treated cotton samples with increasing abrasion cycles. At the end-point of the Martindale test (20,000 cycles), the weight loss of about 14 wt.% was measured for CO_UT. The weight losses of treated samples were lower than untreated cotton fabrics thus obtaining about 11 wt.% for CO_t1 and CO_t3, and 9 wt.% for CO_t6. The presence of the last DBTA layer onto cotton surfaces led to a lowering in their weight loss compared to the same samples without the catalyst. Therefore, the best increase in abrasion resistance was noted for cotton treated with only one TEOS layer and with the catalyst (CO_t1C). This result is probably due to the better adhesion between DBTA and TEOS and between TEOS and substrate.

The influence of TEOS thin films on the tensile properties of cotton fabrics, such as strength and elongation at break, are reported in Table 4. Compared to untreated cotton, sol-gel treated textile samples show mechanical properties slightly changed. In particular, cotton fabrics finished using 0.03 M TEOS sol concentration slightly enhanced the tensile strength values, especially in the presence of three layers, in combination with the catalyst. At these conditions, a maximum weft elongation percentage is registered. No significant variations for elongation (%) performances were observed increasing the number of silica layers. This behavior is probably due to the low TEOS concentration used in the finishing that allows the fibers to be quite free to move and slide between themselves. The increase of the TEOS concentration (0.3 M), simultaneously with the number of layers, does not permit to observe improvements either in tensile strength and in elongation results. Indeed, under these conditions, both mechanical properties are generally lower than the one observed for 0.03 M sol concentration.
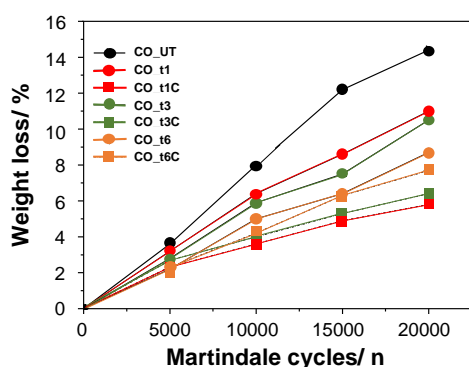
Figure 3. Weight loss (wt.%) of CO_UT and CO_t samples from 1 to 6 silica layers, with and without DBTA, as a function of Martindale cycles.

These results are in agreement with the influence of finishing on the substrate rigidity. For higher TEOS concentrations, polymerization of inorganic coating onto the textile fabrics results in a rigid layer that prevents the movement of the fibers, thus decreasing both the tensile strength and the elongation of the yarn.

Table 4. Tensile strength and elongation for untreated and treated cotton fabrics with the increasing number of layers and in the presence of the catalyst, in both warp and weft directions (standard deviation lower than ±3%). The best results are highlighted in bold.

		CO_UT	CO_t1	CO_t3	CO_t6	CO_t1C	CO_t3C	CO_t6C
Tensile strength (N)	Warp	240.3	325.2	302.4	317.9	317.2	*357.1*	282.3
	Weft	265.5	225.5	*326.6*	302.4	250.3	230.2	306.7
Elongation (%)	Warp	17.0	*17.5*	16.3	15.5	16.3	16.3	14.5
	Weft	16.0	15.3	17.8	16.3	16.7	**17.9**	16.1
		CO_UT	**CO_T1**	**CO_T3**	**CO_T6**	**CO_T1C**	**CO_T3C**	**CO_T6C**
Tensile strength (N)	Warp	240.3	207.3	190.9	150.0	200.1	185.0	150.7
	Weft	265.5	220.1	222.4	125.5	205.7	203.1	179.2
Elongation (%)	Warp	17.0	16.8	13.8	7.5	15.2	13.8	10.5
	Weft	16.0	13.9	12.2	11.0	14.0	13.9	13.5

4. Conclusions

The strategy performed for the development of TEOS thin coatings for application onto cotton fabrics according a multi-layer architecture (1 to 6 layers) for the protection of cultural heritage textiles was described in this study. The influence of two TEOS concentrations, the role of the multilayer architecture and the effect of the DBTA catalyst as the last layer on the properties of cotton fabrics were thoroughly investigated. Treated textiles revealed good adhesion of the multi-layered silica architecture. The presence of TEOS layers onto cotton fabrics and of Si and Sn were investigated by ATR-FTIR spectroscopy and SEM-EDS characterization, respectively. The best performances in terms of washing fastness and thermal stability are shown by the cotton samples treated with the higher TEOS concentration. However, the cellulose samples treated with the lower silica concentration revealed higher abrasion resistance and mechanical properties than that showed by the cotton textiles treated with higher silica coating concentration. With increasing the number of silica layers onto cotton fabrics, both the durability and the thermal stability of final textiles increased. Moreover, durability and abrasion resistance of silica coatings are enhanced by the presence of the catalyst as the last layer, while the latter results in improved thermal stability of the coatings contained the lower TEOS concentration. Experimental findings demonstrated the efficiency of the sol-gel technique in the enhancement of specific properties of textile materials. The developed silica coatings represent reliable alternatives to

existing materials thus highlighting the potential use of the sol-gel technique in the effective protection on cellulose-based polymer in cultural heritage textiles.

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