Abstract

In this work the sol-gel synthesis of silica thin films and a novel multistep process consisting of 1-6 consecutive depositions of tetraethoxysilane (TEOS) onto cotton fabric are presented: samples with a different number of silica layers, with the last one alternately consisting of DBTA (Dibutyltindiacetate) catalyst, were obtained. The interaction of sol–gel derived silica coatings and the textiles fabrics were studied by changing two process variables: the TEOS concentration and the presence or absence of the catalyst.

1. Introduction

Sol–gel techniques based on a tetraethoxysilane (TEOS) precursor are promising and practical to prepare the silica films, due to their low-temperature and cheap processing, and because they are suitable to obtain homogeneous films on a large area substrates. Although the gelation process of TEOS has been widely studied, the available information is limited to sol–gel systems with typical catalysts such as acids or bases [1,2]. The aim of this work is an investigation on the catalyst-amount-layers relationships of cotton fabrics treated with silica precursor. The effects of the DBTA (Dibutyltindiacetate) used as catalyst during the alkoxide reaction and the silica amount applied by sol–gel treatment on the thermo-oxidative behavior of the treated fabrics were deeply studied [3,4]. FT-IR ATR spectroscopy, SEM analysis, thermal and thermo-oxidative stability, washing fastness, flammability and mechanical properties of the sol-gel treated cotton fabrics have been also investigated.

2. Experimental

Scoured and bleached cotton fabric was washed in 2% non-ionic detergent and then rinsed several times with deionized water, dried and put into drier for storage. Tetraethylorthosilicate (TEOS, ≥ 98%, sol-gel precursor), Dibutyltindiacetate (DBTA, condensation catalyst), hydrochloric acid and ethanol were used without further purification. The sol solutions were synthesized by TEOS controlled hydrolysis in HCl solution and ethanol at room temperature, to obtain a 0.3 M sol. A 0.03 M TEOS solution was produced by dilution of the previous 0.3 M solution. The DBTA catalyst solutions were obtained by adding 10% V/V, on used alkoxide precursor amounts, in pure ethanol, and applied on the last dried layer of the sol. The TEOS: DBTA and the TEOS: HCl molar ratios were set to 1:0.06 and 1:0.013, respectively. The cotton fabrics were impregnated with the hybrid sol and afterward passed through a two-roll laboratory padder in order to achieve 70% wet pick-up. After drying at 80°C for 10 min, the fabric sample was either re-coated with the same sol solution, to form a new layer, or treated with the catalyst and then subjected to thermal curing. Two series (0.03M and 0.03M TEOS) of fabrics characterized by a different number of layers (1, 3, and 6) were prepared with and without the condensation catalyst DBTA. Each sample was coded as nL
Gravimetric tests results for the textile fabrics treated by sols at different concentrations, with and without catalyst, show a linear enhancement of the add-on % as a function of the number of applied layers up to 0.64% and to 14.3 % for 0.03 M and 0.3 M TEOS solutions, respectively, irrespective of the use of DBTA catalysts. The FT-IR ATR spectra of the untreated and treated cotton fabrics are shown in Figure 1. Deposition on the film is confirmed by presence at around 1200 cm⁻¹, 953 cm⁻¹, 796 cm⁻¹ of absorption bands assigned to Si-O stretching vibration shoulder, Si-OH stretching, Si-O-Si symmetric stretching, respectively. The band expected at 1018 cm⁻¹ is overlapped with a broad band between 1050 and 980 cm⁻¹ attributed to characteristic peaks of cellulose. A similar behavior of the above mentioned characteristic peaks is observed for 0.03M TEOS treated fabrics: in this case, transmittance percentage differences between untreated and treated samples are smaller than the former, certainly because of the lower concentration of the deposited silica finishing.

3. Results and discussion

Silica thin film adhesion on the cotton fabric surface was successfully confirmed by SEM and EDX elemental analysis measurements. EDX shows a uniform and homogeneous distribution of Si on all the two silica concentrations with/without catalyst and the presence of Sn for the DBTA treated samples.
samples. As expected, the Si content is higher in 0.3 M TEOS treated cotton samples than in 0.03M; more, with the increasing of the number of layers, the Si content is obviously higher, and when the catalyst was used, the Sn amount followed an incremental trend, which was related to the initial amount of TEOS applied.

TGA analysis (subsequently corroborated by the results of DSC analysis) for 0.3 M TEOS finished cotton samples shows no complete volatilization of the samples in air, and a percentage of solid residue remains at 600°C after the decomposition of the substrate, which quantity increases with the number of TEOS layers up to 24.7 % for six layers, suggesting that char formation is related to the finishing treatment. The DBTA catalyst seems not to aid the solid residue formation, and its deposition onto the last TEOS layer reduces the char formation. The 0.03M TEOS finished cotton samples show lower char yield, the presence of catalyst slightly enhancing its formation compared to the samples prepared without. The silica network structure and the thermal stability of silica finished cotton are probably related: as the degree of the silica crosslinking increases, the thermal stability of silica finished cotton increases as well.

Silica treated cotton fabrics were subjected to a series of washings (up to 5 cycles) in order to assess the durability of the silica coating. After every washing the residual add-on % was evaluated. The loss of silica was in the range 1-3% for the fabrics treated with 0.3 M and with 0.03 M TEOS without catalyst. When the DBTA catalyst was included in the coating process, the average loss of silica was comparatively lower, below 1% for all samples. These results and the IR absorption peaks referable to the band cited above, which were already present after five washing cycles, confirm that the silica coating is firmly attached to the fiber surface, irrespective of the number of layers, and that the use of the catalyst enhances the durability of the coating.

After samples direct combustion by a flame, the percent weight loss for the untreated sample was around 99%, whereas at a TEOS concentration of 0.03 M some slight improvement with increasing layers number has been detected. 0.3 M TEOS samples showed the best performances, with a weight loss of around 85% for the six layers finished samples. The presence of the catalyst had a negative impact on the outcome of the test, for all molar concentrations, probably because the protective role of the films deposited on the cotton surface that promote the char formation instead of the production of volatile species that could give a further combustion. The influence of the sol thin films on the physical properties of the treated cotton fabrics was also investigated. Results of Martindale tests carried out for 0.3 M TEOS treated cotton fabrics resulted in broken samples for less than 5000 cycles, and the simultaneous crumpling of the wool abrading device. The presence of a thick ceramic oxide coating probably creates a too abrasive surface towards wool. However, it was observed that while at 25,000 cycles a weight loss close to 16 wt.% was obtained for the untreated sample, the weight loss of the samples treated with six layers of 0.03 M TEOS was of 10 wt.%. These findings give clear evidence that the TEOS treatment significantly improves the abrasion performance. The tensile strength tests carried out for 0.03 M TEOS samples showed a maintenance or a slight enhancement of mechanical characteristics with increasing the number of layers, with a maximum in vertical and horizontal tensile strength for the samples with three layers and with the catalyst. Both vertical (warp) and horizontal (weft) elongation values did not show a significant variation when the number of silica layers increase, although a maximum weft elongation percentage is reached for the three layers sample. At higher TEOS concentration (0.3 M), the increased number of layers increases substrate rigidity. Tensile strength is generally lower than the one detected for 0.03M TEOS samples. Maximum weft elongation is again observed for the three layers samples, while warp elongation shows a reduction when TEOS layers increase, and the values are always lower than the untreated sample. For higher TEOS concentrations, polymerization and grafting of the precursor onto the substrate result in a rigid layer that prevents the movement of the fibers, thus decreasing both the tensile strength and the elongation of the yarn proportionally to the number of layers.
4. Conclusions

Silica thin film on the cotton fabric surface was successfully performed, as confirmed by the results of FT-IR-ATR, SEM and EDX elemental analysis measurements. The coating layers present a good adhesion to the textile substrate, as well as good durability. TGA-DTG and DSC analyses of the treated cotton samples revealed that these sol-gel treatments cause a great thermal stability to cellulose fabrics: indeed, the fabric covered by the silica thin film was able to produce a greater amount of char as compared to the untreated fabric both in nitrogen and in air atmosphere. The investigation also showed a good washing fastness for all samples, and the presence of the silica coating after one and five washing cycles onto cotton substrate was confirmed by good results of residue percentage obtained after fire tests. These results are in good agreement with the ones of abrasion resistance: all the tested 0.03 M TEOS finished fabrics showed a remarkable improvement of abrasion resistance, a lower weight loss and higher endpoint of Martindale test than untreated samples. Tensile strength and elongation percentage results gave the best for three layers samples for both finishing concentrations. The DBTA catalyst doesn’t seem to induce significant contributions to the silica film characteristics and its role has to be further investigated.

References