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Heat and moisture transfer in sol–gel treated cotton fabrics

Jenny Alongi · Giulio Malucelli

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Abstract Cotton fabrics have been treated by sol–gel processes in order to produce an inorganic coating on fibres, able to modify their thermal conductivity under an irradiating flow. To this aim, fabric specimens with different silica content have been tested following the ISO 6942 standard in order to establish the effect of the coating on coupled heat and moisture transfer through the cotton fibres. The collected results have been compared with those obtained by an optimized method using a cone calorimeter as the heating source. By this latter approach, it has been demonstrated that sol–gel cotton treated fabrics with high moisture uptake possess a significantly lower thermal conductivity with respect to cotton alone.

Keywords Heat · Moisture · Cotton · Sol–gel treatments · Silica coating · Cone calorimeter

Introduction

Heat and moisture transfer in porous media represents one of the most interesting research areas for several applications in the scientific and engineering fields, such as civil engineering, energy storage and conservation, as well as functional clothing design, etc. [1, 2]. Since the first pioneering attempt by Henry [3], many theoretical models based on numerical approaches have been proposed [4–8]; however, few experiments on coupled heat and moisture transfer in fibrous materials have been carried out and published in the literature so far [9]. In particular, to the best of our knowledge, only very few studies have been reported on the influence of heat transfer coupled to moisture transfer in cotton fabrics under a simulated fire [10, 11]. As an example, the model-based approach for determining the properties of flame-protective garments has been generally focused only on the evaluation of heat exposure effects on the human skin, neglecting the moisture effect. In other words, the percentage of the body surface subjected to first-, second- and third-degree burns has been measured under a selected heat flow only, using different approaches [12]. Indeed, a thorough study on the characteristics of flame-protective garments should be based on an overall comprehension of all the key factors involved in a burning process. The effectiveness of a protective clothing depends on the nature of various substrates (i.e. natural, artificial or synthetic fibres/fabrics with their chemical characteristics), and on combination of them into layers, as well as the cut, design/texture and positioning of belts and braces. These aspects are well defined by the different standards issued by the International Organization for Standardization in relation to the application fields. In particular, the standards for the protective garments of fire fighters specified by ISO 6942 [13], which is based on two complementary methods for determining the behaviour of materials for heat protective clothing subjected to heat radiation, are obviously stricter than the others. The tests carried out according to the above two methods serve to classify materials; however, to be able to make a statement or prediction as referred to the suitability of a material for protective clothing, it is necessary to take into account additional criteria, as claimed by the same Organization. Indeed, the ISO 6942 standard is very useful for the selection of materials appropriate for fire fighters, but it does not consider the effect of moisture within the fabric

J. Alongi · G. Malucelli (✉)
Dipartimento di Scienza Applicata e Tecnologia,
Politecnico di Torino, Viale Teresa Michel 5,
15121 Alessandria, Italy
e-mail: giulio.malucelli@polito.it

since it is supposed that all the substrates taken in consideration can reach the maximum absorbed moisture content at 20 ± 2 °C, 65 ± 2 % relative humidity within 24 h.

For all the above reasons it seems necessary to evaluate the coupled effect of the moisture and heat during the irradiation of hygroscopic porous materials, such as cotton fabrics, in order to get a wider comprehension of the occurring phenomena. Indeed, the heat transfer can be related to three different phenomena, i.e. *conduction* by the solid material of the fibres in the presence of air, *radiation* promoted by the large temperature difference and *convection* due to air penetration within the porous material. Meanwhile, moisture transfer involves vapour diffusion within the texture, moisture diffusion within fibres (sorption/adsorption), condensation/evaporation at fibre surface, and liquid transfer inside the fabric promoted by capillary effects and a function of pore size distribution [6].

These aspects have been widely discussed by Zhu and Li [10] with particular attention to the possible application of flame resistant cotton fabrics for personal protective clothing: in particular, the pyrolysis of wet cotton fabrics and the combined heat and moisture effects on their thermal and flame retardancy performances have been investigated.

Furthermore, Zeronian et al. [11] have found that cotton flammability linearly depends on its moisture content as assessed by measuring the limiting oxygen index (LOI). It is suggested that the moisture present in the treated samples does not reduce flammability by entering into solid and/or gaseous phase reactions, but by simply absorbing thermal energy owing to the endothermic process of heating and vaporization.

Pursuing the above research lines, this article is aimed to investigate the effect of coupled heat and moisture transfer on cotton fabrics subjected to sol–gel treatments. Indeed, the use of sol–gel processes for obtaining oxidic phases (e.g. silica, titania, zirconia and alumina) in order to increase the flame resistance of polyester and cotton has been recently reported [14–20]. Such treatments proved to be responsible for an overall enhancement of the thermal and fire stability of the fabrics, which was ascribed to moisture content of the inorganic coatings on fabric surface.

In this article, sol–gel treated cotton fabrics with different silica content have been tested following the ISO 6942 standard. The collected results have been compared with those obtained by an optimized method based on a cone calorimeter as the heating source. Furthermore, an experimental setup has been proposed for evaluating the thermal insulating efficiency of the inorganic coatings prepared by sol–gel processes and its dependence on the moisture content.

Experimental part

Materials

Cotton fabrics (purchased from Fratelli Ballesio, Italy) with a density of 100, 200 and 400 g/m^2 (hereinafter coded as CO100, CO200 and CO400, respectively) and the same texture/design were used as received. Tetramethoxysilane (TMOS), water, ethanol and dibutyltindiacetate (all reagent grades) were purchased from Sigma-Aldrich and used as received.

Sol–gel treatments performed on cotton fabrics

Silica phases were synthesized by the sol–gel method using TMOS as silica precursor. A pure silica sol was prepared via hydrolysis: a mixture containing TMOS, ethanol and distilled water was stirred at room temperature for 10 min. At constant ethanol:TMOS molar ratio, kept at 0.07 (this value is adequate to ensure complete miscibility of the three liquids), different TMOS:H_2O molar ratios (i.e. 1:2, 1:1 and 2:1) were investigated (hereinafter coded as COXXXTMOS12, COXXXTMOS11 and COXXXTMOS21, respectively). Dibutyltindiacetate (0.9 wt%) was added to the sol solution as the condensation catalyst. Then, the cotton fabrics were impregnated at room temperature in the silica sol (1 min) and subsequently thermally treated at 80 °C for 15 h in a gravity convection oven.

Characterization

The flame retardancy of the pure fabrics and of their sol–gel treated counterparts was measured according to the ISO 6942 standard that specifies two complementary methods (namely, A and B), as mentioned in the "Introduction", for assessing the behaviour of materials for heat protective clothing subjected to heat radiation. Method A serves for visual evaluation of any changes in the material after the action of heat radiation, while the protective effect of the materials is determined by method B. In this study, method B was used in order to assess the heat transmission factor (TF, %, defined as the fraction of heat transmitted across a specimen exposed to a heating source of 20 kW/m^2), and the density of incident heat flow (Q, kW/m^2), that represents the amount of incident energy per time unit on the specimen surface exposed to the heat flow. These two parameters were evaluated measuring the time (expressed in s) necessary to get a temperature increase of 12 ± 0.1 and 24 ± 0.2 °C (t_{12} and t_{24}, respectively), as assessed by the calorimeter. Each measurement was repeated three times in order to have reproducible data and standard deviation (σ) was reported for each value.

The collected results were compared with those obtained by an optimized procedure for fabrics using a cone calorimeter as the heating source. This set up was proposed for evaluating the thermal insulation of the inorganic coatings prepared by sol–gel processes. In particular, fabric specimens with a defined size ($100 \times 100 \times 0.5$ mm^3) were placed between two ceramic pads holed in the centre and kept 25 mm far from the cone source. Two separated thermocouples (stainless steel sheathed K-type thermocouples with 1.5 mm outer diameter), connected with the heating source (cone calorimeter), were used for measuring the temperature of the front and back faces of the sample, respectively.

During the measurement, each sample was irradiated by a 10 kW/m^2 heat flow and the temperature profiles of the front and back faces of the specimen were monitored and acquired. The temperature difference ΔT was plotted as a function of time. In order to establish a comparison between pure fabrics and sol–gel treated counterparts, the temperature difference at a certain time (200 s) was also assessed. Each measurement was repeated three times in order to have reproducible data and the error was ±0.5 °C. The experimental apparatus is depicted in Fig. 1.

Prior to such tests, each sample was conditioned in a climate chamber at 23 ± 1 °C and 50 ± 1 % relative humidity for different times (24, 48 and 72 h, respectively). Some of the samples were also dried at 80 °C for 48 h in a vacuum oven.

In order to determine the moisture content of pure and sol–gel treated cotton fabrics, that can significantly influence the thermal conductivity of these materials, a Karl-Fisher titrator (Mettler Toledo, model V20) was used: small pieces (ca. 1 g) were heated up to 100 °C and the moisture content was determined by using a mixture of methanol, potassium metabisulphite and I_2 as the titration system. The error was 0.5 %.

Results and discussion

Previous works have shown that silica is an efficient flame retardant finishing system for cotton [14–20]. In particular, measurements by cone calorimetry have demonstrated that a homogeneous and compact silica thin film, deposited on cotton fibres by sol–gel processes, is able to increase the time to ignition and to decrease the heat release rate of cotton when the fabric is irradiated with a 35 kW/m^2 heat flow. The above improvements have been achieved although the condensation reaction of the alkoxide precursor (namely, TMOS) was always incomplete, regardless of the specific TMOS:H_2O molar ratio. Indeed, as already supported by ^{29}Si-solid state NMR measurements [15], the degree of condensation is rather high (ca. 80 %) for all the formulations. Furthermore, it has also been demonstrated in the same paper that only a 1:1 molar ratio between TMOS and water proved to be very efficient for decreasing the cotton flammability in terms of combustion behaviour: cone calorimetry tests have shown that this composition is able to increase the time to ignition from 18 to 28 s and decrease the heat release rate down to 82 from 93 kW/m^2 during the combustion of cotton. Some plausible explanations can be referred to both the hydrophilic character and the porosity of the coating, as well as its capability to entrap moisture, as clearly reported in the literature [5].

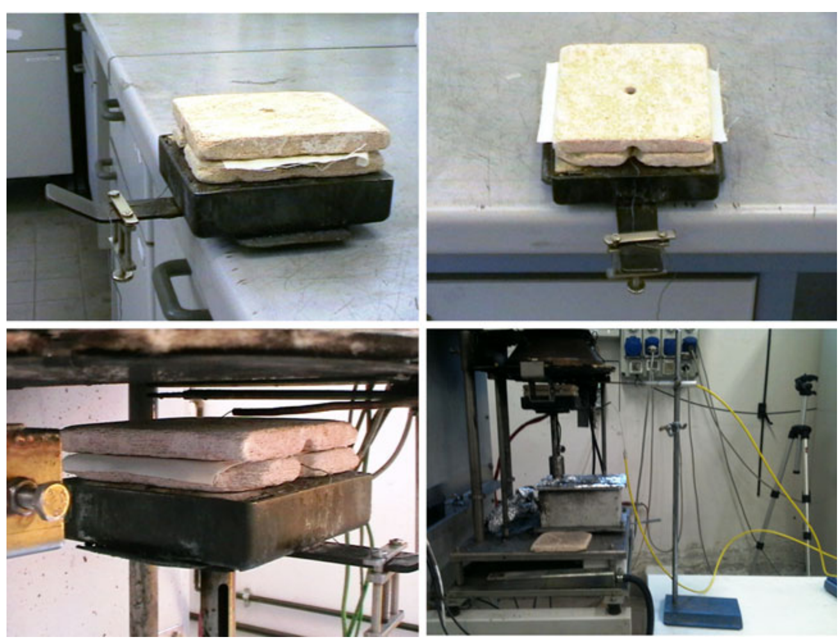

Fig. 1 Experimental set up for evaluating the thermal insulation efficiency of cotton fabrics

Table 1 Collected data from the tests performed according to ISO 6942

Sample	t_{12}/s	t_{24}/s	TF ± σ/%	$Q \pm \sigma$/kW/m^2	Moisture content/%[a]
CO200	5.3	10.5	62.9 ± 1.1	12.6 ± 0.2	6.4
CO200TMOS12	5.2	10.1	67.9 ± 1.4	13.4 ± 0.3	5.2
CO200TMOS11	5.5	10.6	64.0 ± 1.3	13.0 ± 0.3	7.1
CO200TMOS21	5.0	9.8	69.9 ± 1.4	13.9 ± 0.4	5.4

[a] By Karl-Fisher titration

Indeed, during the initial degradation of cotton, immediately before the combustion, water plays an important role as is capable to delay the ignition of cellulose, diluting the volatile products derived from its degradation; therefore, it is reasonable to hypothesize that the higher the moisture content, the higher is the time to ignition. This hypothesis has also been recently confirmed by changing the type of the metal alkoxide precursor employed in the sol–gel process [15]: among the different explored systems, silica resulted the most efficient coating for increasing the time to ignition of cotton, also because it is able to entrap the highest moisture content as compared to titania, zirconia and alumina.

Hence, the above study has pointed out that moisture can play an effective role in the evolution of cotton combustion in the gas phase. Furthermore, moisture itself could also be responsible of a substantial change of cotton's thermal conductivity that is directly related to its flame retardancy properties.

In this study, the flame retardancy of cotton alone and that of samples treated with different TMOS:H_2O molar ratios (namely, 1:2, 1:1 and 2:1) has been measured according to the ISO 6942 standard (method B) for assessing the behaviour of such materials when subjected to heat radiation. The collected data are given in Table 1: they show that two out of three sol–gel treated samples are characterised by somewhat higher values of both the heat transmission factor and the density of incident heat flow with respect to pure cotton (measured at t_{12} and t_{24}). Namely, CO200TMOS12 and CO200TMOS21 show a larger increase of TF and Q in relation to their lower moisture content. Indeed, when the latter samples are irradiated, the heat is partially used for evaporating the water adsorbed on the cotton surface or entrapped in the ceramic coating and then transmitted to the fabric.

On the basis of the results obtained from the ISO 6942 standard and pertaining to the combustion behaviour observed for the sol–gel treated samples, we have focused our further investigation only on the system treated with equimolar ratio of TMOS and water, using a different experimental apparatus. By this way, it has been possible to check the influence of coupled heat and moisture transfer:

Fig. 2 Temperature profiles of the three cotton fabrics with different density

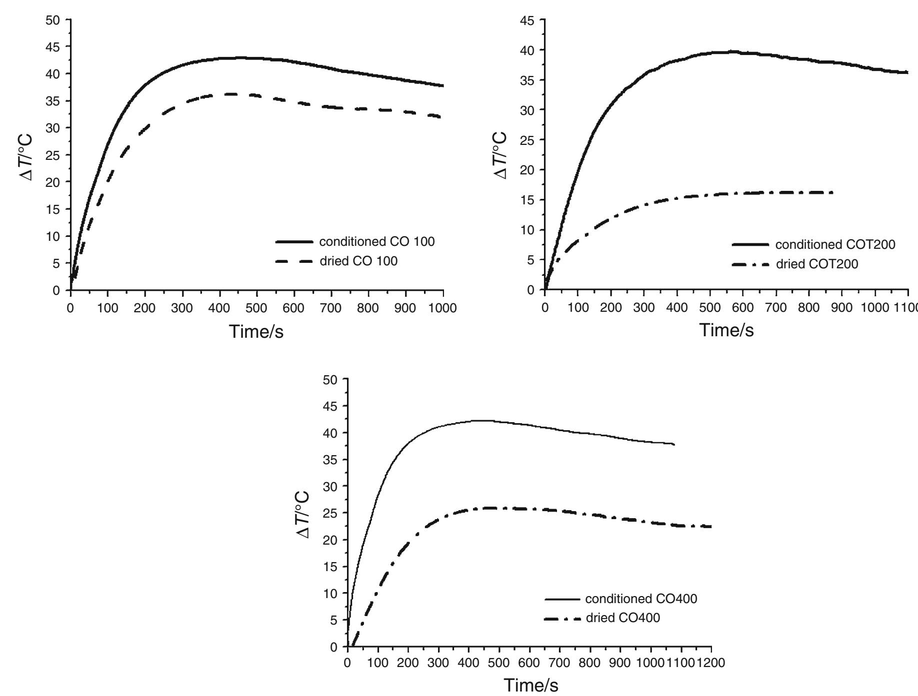

Table 2 Collected data for different pure cotton fabrics performed by cone calorimeter

Sample		ΔT at 200 s/°C	Moisture content/%[a]
CO100	Conditioned 48 h	38	6.6
	Dried	28	4.3
CO200	Conditioned 48 h	34	8.0
	Dried	12	4.8
CO400	Conditioned 48 h	38	8.2
	Dried	19	5.0

[a] By Karl-Fisher titration

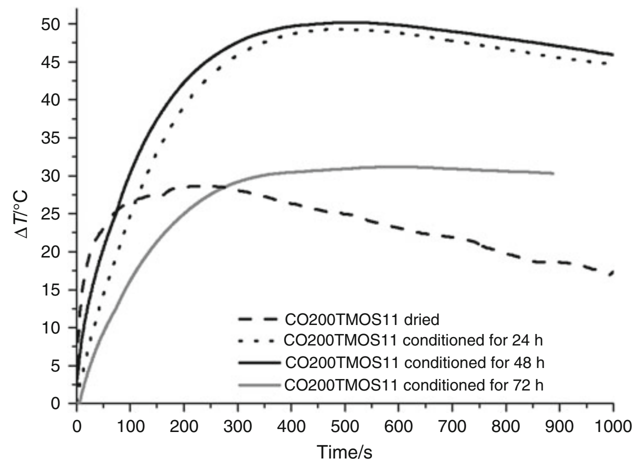

Fig. 3 Temperature profiles of CO200 sol–gel treated fabrics as functions of the conditioning set ups

as described in the "Experimental part", pure cotton and treated samples have been irradiated under the cone source and the corresponding temperature profiles of the front and back faces of the specimens have been acquired. In this manner, an indirect measurement of the thermal conductivity of such fabrics has been performed.

First of all, the three cotton fabrics with different density (namely, CO100, CO200 and CO400) have been compared: Fig. 2 plots ΔT as a function of time for each sample conditioned for 48 h or dried. It is noteworthy that the ΔT profile is similar for all the samples, regardless of their density and conditioning procedure: at the beginning ΔT increases almost linearly as a function of time, then after reaching a horizontal plateau after ca. 200 s. The ΔT data referred to the above time are listed in Table 2. Since the temperature of the front face of the specimen is determined by the geometry of the cone apparatus and fixed at the experimentally measured values of 360 °C, it is reasonable to assume that the temperature of the back site is responsible of the measured ΔT.

As evident from the data in Table 2, independently of their density, all the samples conditioned for 48 h have higher moisture contents and consequently higher ΔT values at 200 s with respect to the dried counterparts. Larger ΔT values at 200 s mean that the temperature of the back site is lower for the samples containing higher moisture, since the heat is partially involved in the moisture evaporation. As a consequence, the samples having a higher moisture content possess a lower thermal conductivity.

In order to further evaluate the effect of moisture on this kind of measurements, cotton fabrics with a density of 200 g/m^2 have been conditioned in a climate chamber at 23 ± 1 °C and 50 ± 1 % relative humidity for 24, 48 and 72 h, respectively.

The above fabric density is typical of the clothing for protective garments. Table 3 summarises the collected data.

The moisture content found by Karl-Fisher titration shows that cotton absorbs moisture within the first 48 h of conditioning in the climate chamber; then after, its content remains practically unchanged. Once again, ΔT turns out to be influenced by moisture content. After the sol–gel treatment (CO200TMOS11 sample), the water adsorption still occurs within 48 h and the resulting temperature profile depends on the moisture content (Table 3). In addition, regardless of the adopted experimental conditions (i.e. dry or conditioning for 24, 48 and 72 h), the ΔT curves reported in Fig. 3 show similar profiles. The main difference between untreated and treated fabrics is their moisture content (Table 3): the inorganic coating deposited on the fibres is able to entrap a higher

Table 3 Collected data for CO200 and sol–gel treated fabrics performed by cone calorimeter

Sample	CO200		CO200TMOS11	
	ΔT at 200 s/°C	Moisture content/%[a]	ΔT at 200 s/°C	Moisture content/%[a]
Dried	12	4.8	28 (+16)	5.6
Conditioned 24 h	32	6.3	39 (+7)	7.1
Conditioned 48 h	34	8.0	42 (+8)	9.2
Conditioned 72 h	26	7.8	44 (+18)	9.6

[a] By Karl-Fisher titration

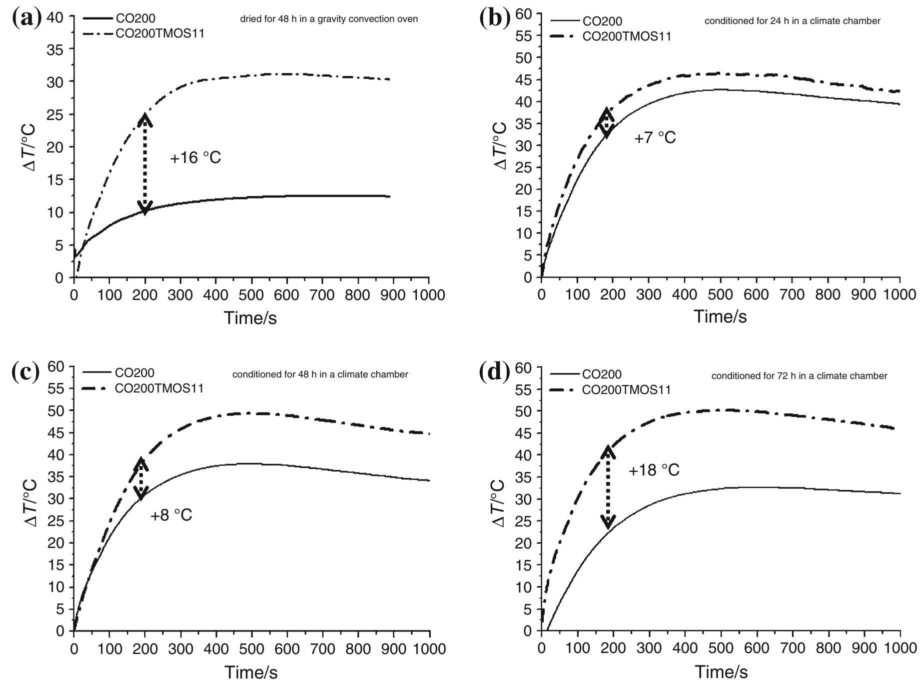

Fig. 4 Comparison between temperature profiles of CO200 and CO200 sol–gel treated fabrics: **a** dried samples, **b**–**d** conditioned for 24, 48, and 72 h, respectively

moisture content with respect to cotton alone. As an example, after 48 h of conditioning, the water content is 8.0 and 9.2 % for pure and sol–gel treated fabrics, respectively. Once again, the higher the water content, the higher is ΔT, i.e. the temperature of the specimen back face is lower. The above measurements show that the specimen back face of the treated samples is always cooler than that of the pure cotton, as well depicted in Fig. 4, where their ΔT profiles are plotted as functions of time according to the different conditioning set ups. On the basis of these results, we can conclude that the treated samples are efficient thermal insulators since the lower the temperature of the specimen back face, the lower is the thermal conductivity.

In conclusion, the inorganic coating prepared through sol–gel processes seems to be an efficient thermal insulator for cotton fabrics due to the higher moisture entrapped that can partially dissipate the heat under irradiation. As a consequence, during the combustion of the cotton, moisture is able to act in a twofold manner: immediately before the combustion, it delays the ignition of cellulose, diluting the volatile products derived from its degradation, as well as it cools down the system. This double feature of the inorganic coating could explain the increase of time to ignition and thus the enhancement of cotton flame retardancy observed in the previous works.

Conclusions

In this article, the thermal insulation efficiency of sol–gel derived silica coatings on cotton fabrics has been investigated. To this aim, the ISO 6942 standard and an optimized method using a cone calorimeter as the heating source have been exploited and the results in terms of coupled heat and moisture transfer compared.

The presence of the inorganic coating proved to significantly influence both heat and moisture transfer within cotton fibres. Indeed, the thermal conductivity of the sol–gel treated samples has been found to be strongly affected by the conditioning set up of the samples and consequently by the moisture uptake.

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