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Cotton fabrics treated with novel oxidic phases acting as effective smoke suppressants

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ABSTRACT

Sol–gel processes have been applied to cotton fabrics in order to coat the fibres with a silica film, able to improve their thermo-oxidative resistance and their combustion behaviour under the irradiative heat flow of a cone calorimeter. To this aim, tetramethoxysilane, inorganic precursor of the silica phase, has been employed alone or coupled with species having either smoke suppressant features (namely, zinc oxide, zinc acetate dihydrate and zinc borate) or well known flame retardant properties (like ammonium pentaborate octahydrate, boron phosphate, ammonium polyphosphate and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide). In addition, the use of barium sulphate, which is a smoke suppressant and, at the same time, a flame retardant, has been investigated. Cone calorimetry turned out to be a suitable technique for assessing the flammability and smoke production of the treated fabrics (particularly when referring to total smoke release, smoke production rate and CO and CO_2 yields). The composition and morphology of the deposited coatings, assessed by scanning electron microscopy, have been found to influence their combustion behaviour, as well as their thermal and thermo-oxidative stability evaluated by thermogravimetric analysis in nitrogen and air, respectively.

1. Introduction

Smoke has a vague definition, as addressed by Price, Anthony, and Carty (2001): indeed, it is generally considered to be a cloud of particles (individually invisible because of their reduced size), able to scatter and/or absorb visible light. Smoke differs from *fume*, since this latter can be considered as a less opaque form of smoke. During the combustion of a polymer, the production of “combustible gases” (i.e. CO) and “visible smokes” are crucial factors to take in consideration since the loss of visibility due to heavy smoke can hinder escape pathways, while toxic gas concentration (especially at high temperatures) can be very critical. Most likely, since escape time can get benefits from the reduction of the rate and intensity of visible smoke development, the investigation on effective smoke suppressants for polymers becomes a key parameter in the combustion processes of the latter. Visible smoke from burning polymers is usually a consequence of incomplete combustion. Upon heating, at certain temperatures, polymers undergo pyrolysis, thus giving rise to low molecular weight species (Price et al., 2001). These species diffuse from the solid into the gas phase, where they form smoke and other reactive species that further fuel the polymer combustion. Namely, aliphatic species are cracked to small alkyl radicals and grow to form conjugated polyenes or polybenzenoids that react and condense with other unsaturated species to give soot. Meanwhile, the oxidation of carbon to oxides (CO and CO_2) occurs through a competitive pathway to the soot formation. Indeed, the mechanism by which a polymer burns is very complex and the number of the involved parameters is high. Several approaches, that involve certain chemical reactions occurring either in gas phase or in solid and liquid phases, have been developed for reducing the smoke production. The chemical reactions taking place in the solid phase seem to be one of the most promising and encouraging routes, as they allow diluting the combustible polymer content, dissipating heat, insulating and protecting the surface of the combustible substrate and finally promoting the formation of char and modifying the pyrolysis reactions.

Within the above scenario, all the flame retardant systems adopted for natural fibres (such as cotton or viscose) derive from a chemical finishing process, which is able to enhance the flame retardant efficiency and the durability to laundering, according to the chemical nature and cost of the flame retardant itself. These systems may simply consist of soluble salts (i.e. ammonium phosphate and polyphosphate, borate–boric acid mixtures), which can be exploited for non-durable finishes. In some other cases, they may be chemically reactive (i.e. alkylphosphonamide derivatives and tetrakis hydroxylmethylphosphonium salts), thus providing functional finishes for durable flame retardancy; finally, they can

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be utilized as back coatings, which usually comprise a resin-bonded antimony/bromine flame retardant system (Horrocks, 1986, 2001, 2008, 2011; Horrocks, Kandola, Davies, Zhang, & Padbury, 2005). It should be noted that, since the most effective flame retardants contain either phosphorus- or antimony/bromine-based compounds, they generate a perception of unacceptable environmental hazard. Indeed, their use may result in significant effects on toxic potency by modifying combustion efficiency and increasing the yields of smoke and asphyxiant gases. As an example, cotton treated with a bromine/antimony back coating is able to produce a higher amount of carbon monoxide (by a factor of 10) with respect to the untreated fabric in non-flaming conditions at 700 °C (Purser, 2001).

For these reasons, the requirement of safety and eco-friendly systems acting as smoke suppressants or flame retardants or having both the above features is continuously growing. The latter solution seems to be the most promising and appreciable from an economical point of view. Antimony, iron, molybdenum and zinc compounds represent the most promising and efficient systems (Price et al., 2001). On one hand, the use of fillers, classified as *inert* or *active*, on the basis of their apparent smoke suppressant functions, is already documented in the literature for bulk polymers. Such inert fillers as silica, clays and calcium carbonate are able to lower the amount of smoke generated from a given mass or volume of a polymer, by simply diluting or decreasing the amount of combustible substrate present and also by absorbing heat (so that the burning rate slows down). On the other hand, aluminium and magnesium hydroxides behave as active fillers: they differ from the inert counterpart since they give rise to endothermic processes, which are capable to absorb more heat per unit weight, being equal the diluent and heat adsorption functions.

Referring to inert fillers, silica nanoparticles or silica-based coatings can be easily synthesized through sol–gel processes: as clearly reported in the literature, these latter represent a versatile synthetic route based on a two-step reaction (hydrolysis and condensation), starting from (semi)metal alkoxides (tetraethoxysilane, tetramethoxysilane, titanium tetraisopropoxide, etc.), that leads to the formation of completely inorganic or hybrid organic–inorganic coatings at or near room temperature (Sakka, 2003). Recently, our group has demonstrated that sol–gel treatments are able to modify the combustion behaviour of cotton fabrics forming a silica coating able to act as a surface thermal insulator, diluting the combustible polymer content, dissipating heat, hindering the formation of volatile species that fuel further degradation and favouring the formation of char (Alongi, Ciobanu, Carosio, Tata, & Malucelli, 2011; Alongi, Ciobanu, & Malucelli, 2011a, 2011b, 2011c; Alongi, Ciobanu, & Malucelli, 2012a, 2012b, in press).

In the present work, the effect of silica alone or coupled with other active species acting as smoke suppressants on the flammability and smoke production for cotton fabrics has been thoroughly explored. More specifically, the joint effect between silica and tin-, boron- or phosphorus-based compounds has been pursued and assessed. Among these species, only tin-based compounds are classifiable as smoke suppressants (Horrocks, Smart, Nazaré, Kandola, & Price, 2010; Kandare, Kandola, Price, Nazaré, & Horrocks, 2008; Nazaré, Kandola, & Horrocks, 2008; Price et al., 2001), while the other compounds are known for their flame retardant features. In addition, the investigation has been extended to barium sulphate, which exhibits both the characteristics. A deep investigation on the total smoke release, the smoke production rate, and CO and CO_2 yields has been performed by cone calorimetry, in order to evaluate the effect of each type of additive on the smoke production. The obtained results have been related to the morphology of the deposited coatings (assessed by scanning electron microscopy) as well as their thermal stability in inert and oxidative atmosphere (evaluated by thermogravimetric analysis in nitrogen and air, respectively).

2. Experimental

2.1. Materials

Cotton fabrics (CO, purchased from Fratelli Ballesio, Torino, Italy) with a density of 290 g/m^2 were used as received.

Tetramethylorthosilicate (TMOS), water, ethanol, dibutyltin-diacetate (DBTA, condensation catalyst), smoke suppressants (namely, zinc oxide – ZnO, zinc acetate dehydrate – ZnAc and zinc borate – ZnB), flame retardants (namely, ammonium pentaborate octahydrate – APB, boron phosphate – BP, ammonium polyphosphate – APP and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide – DOPO), all reagent grades, were purchased from Sigma–Aldrich and used without any further purification. Barium sulphate (BaS) was purchased from Sigma–Aldrich and used without any further purification both as smoke suppressant and flame retardant.

2.2. Sol–gel treatments performed on cotton

First of all, pure silica phases were obtained from a sol containing tetramethylorthosilicate, distilled water (precursor:water molar ratio = 1:1), ethanol and DBTA (0.9 wt.%); the cotton fabrics were impregnated in the sol solution for 5 min at r.t. and subsequently thermally treated at 80 °C for 15 h using a gravity convection oven.

In addition, in some formulations smoke suppressants or flame retardants were also added to the sol solution (according to their solubility) before adding DBTA (condensation catalyst). All the formulations identified with a sample code CO_Si or CO_Si_X are collected in Table 1.

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

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

2.3. Characterization techniques

The surface morphology of the treated samples was studied using a LEO-1450VP Scanning Electron Microscope (beam voltage: 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. Fabric pieces (5 mm × 5 mm) were cut and fixed to conductive adhesive tapes and gold-metallized.

The thermal stability of the fabrics was evaluated by thermogravimetric (TG) analyses from 50 to 800 °C with a heating rate of 10 °C/min, both in nitrogen and in air (60 ml/min). To this aim, a TAQ500 thermogravimetric balance was used, placing the samples in open alumina pans (ca. 10 mg). The experimental error was 0.5% on the weight and 1 °C on the temperature.

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 carried out under a 35 kW/m^2 irradiative heat flow in horizontal configuration, following the procedure described elsewhere (Tata, Alongi, Carosio, & Frache, 2011). Such parameters as Time To Ignition (TTI, s), Total Heat Release (THR, kW/m^2), peak of Heat Release Rate (HRR, kW/m^2) were measured. Total Smoke Release (TSR, m^2/m^2), peak of Rate of Smoke Release (1/s), Smoke Factor (SF, calculated as PHRR × TSR, MW/m^2) and CO and CO_2 release (g/s) were evaluated, as well. The experiments were repeated four times for each material investigated to ensure reproducible