

Sol–gel treatments on cotton fabrics for improving thermal and flame stability: Effect of the structure of the alkoxy silane precursor

Jenny Alongi*, Mihaela Ciobanu, Giulio Malucelli

Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, sede di Alessandria, V. Teresa Michel 5, 15121 Alessandria, Italy

ARTICLE INFO

Article history:

Received 20 June 2011

Received in revised form 31 July 2011

Accepted 14 August 2011

Available online 22 August 2011

Keywords:

Cotton

Sol–gel processes

Alkoxy silanes

Thermal stability

Flame retardancy

Combustion behaviour

ABSTRACT

Sol–gel treatments have been performed on cotton fabrics in order to promote the formation of a surface silica insulating barrier, able to enhance their thermo-oxidative stability and flame retardancy. In particular, the role of several silica precursors, which differ as far as their structure (number and type of hydrolysable groups, presence of aromatic rings) is concerned, has been thoroughly investigated. The level of silica distribution and dispersion on and within the fabrics was found to depend on the type of precursor employed, as revealed by scanning electron microscopy and elemental analysis. All the precursors were able to favour the char formation in air below 360 °C, as stated by thermogravimetric analysis: in particular, the highest thermal stability was achieved in the presence of precursors bearing aromatic rings. Indeed, both flammability resistance and combustion behaviour of the treated fabrics were remarkably enhanced.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

It is well documented that nanometric fillers can significantly enhance the flame retardancy of polymers, since thermal degradation and combustion mechanism of the latter dramatically change in the presence of such additives (Horrocks, 2008; Jiang, 2010; Wilkie & Morgan, 2008). Scientists have hypothesized and proposed several action routes exerted by the nanofillers: in particular, it has been observed that a surface insulating barrier, which includes a high nanoparticle content, is formed upon pyrolysis and combustion of the polymer. Indeed, this barrier is thought to be responsible for improving flame retardancy (Lewin, 2006; Tang & Lewin, 2008). The most shared hypothesis on the formation of such a barrier in bulk nanocomposites lays on the migration of the nanoparticles on the surface, thus forming a continuous ceramic layer that prevents the heat and oxygen transfer from the ambient to the bulk polymer (Kashiwagi et al., 2000; Lewin, 2003, 2006; Tang & Lewin, 2008), as confirmed by XPS measurements (Schmitt & Gardella, 1986; Thomas & O'Malley, 1981).

These findings have been observed for the nanocomposites containing either natural or organo-modified phyllosilicates (clays) or silica. For this latter system, Kashiwagi et al. (2000) have investigated the effect of silica particles added to polypropylene and polyethylene oxide by melt blending and studied their flame retar-

dant efficiency as well as kinetics and mechanism. It was found that the kinetics relies on a physical effect (instead of a chemical “driving force”), due to the silica segregation within the outermost polymer layers, which provides thermal insulation against the degradation of the volatile products moving from the polymer to the surface. Furthermore, cone calorimetry data (heat release and mass loss rate) have demonstrated that the silica synthesized through sol–gel processes (i.e. by means of a bottom-up approach) is more efficient than fumed and fused silica submicro- and nanoparticles, probably because of a better control of their size and distribution.

The use of sol–gel processes for obtaining silica nanoparticles is well documented in the literature. Several papers have recently investigated the possibility to reduce the flammability of different polymers, such as epoxies (Chiang & Chang, 2008; Chiang & Ma, 2002; Chiang, Wang, Ma, & Chang, 2002; Hsiue, Liu, & Liao, 2001; Liu & Chou, 2005; Liu, Wu, Chiu, & Ho, 2003; Yu, Liu, & Liu, 2010) and phenolic resins (Chiang & Ma, 2004; Chiang, Ma, Wu, & Kuan, 2003), polymethylmethacrylates (Chiang & Chiu, 2009; Messori et al., 2003), polyesters (Ji, Wang, Zhang, Kong, & Xia, 2009) and polyimides (Liu, Gao, Wang, Li, & Xu, 2002), by exploiting silica phases derived from sol–gel processes. Therefore, since silica coatings can be extremely efficient as insulating barrier on the surface of any substrate and in particular on fabrics, we recently focused on the use of sol–gel treatments performed on cotton fabrics.

We have already demonstrated that two common silica precursors, namely tetramethylorthosilicate and tetraethylorthosilicate, are effectively suitable for enhancing the flame retardant properties of cotton fabrics (Alongi, Ciobanu, Carosio, Tata, & Malucelli,

* Corresponding author. Tel.: +39 0131229337; fax: +39 0131229399.
E-mail address: jenny.alongi@polito.it (J. Alongi).

2011; Alongi, Ciobanu, & Malucelli, 2011a, 2011b, 2011c). Nevertheless, such investigation has never been extended to assess the effectiveness of several commercially available alkoxysilanes, which differ in their chemical structure (i.e. number and type of hydrolysable groups, possible presence of aromatic rings in their backbone). Therefore, in the present paper we present a systematic investigation on the structure–property relationships of cotton fabrics treated with these silica precursors. The effects of both the chemical structure of the used alkoxides and the morphology of the silica phases formed after the sol–gel treatment on the thermo-oxidative stability, flammability and combustion behaviour of the treated fabrics are deeply investigated.

2. Experimental part

2.1. Materials

Cotton fabrics (CO, purchased from Fratelli Ballesio, Torino, Italy) with a density of 200 g/m² were used as received. Several silica precursors (the structure of which is schematized in Table 1), water, ethanol and dibutyltinodiacetate–DBTA, (all reagent grade) were purchased from Sigma–Aldrich and used without any further purification.

2.2. Sol–gel treatments on the cotton fabrics

Pure silica phases were synthesized on the cotton fabrics through sol–gel processes. More specifically, a mixture containing the precursor, distilled water (precursor: water molar ratio = 1:1), ethanol and DBTA (0.9 wt.%) was stirred at room temperature for 10 min. Then, cotton fabrics were impregnated at room temperature in the sol solution (1 min) and, subsequently, thermally treated at 80 °C for 15 h using a gravity convection oven. Finally, all the fabrics were washed for 1 h in distilled water at 60 °C in order to eliminate the unreacted precursor.

Hereinafter, the treated cotton samples will be identified by using the code of the inorganic precursor, as reported in Table 1.

2.3. Characterization techniques

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. A Pyris1TGAQ500 analyzer was used, placing the samples in open alumina pans (ca. 10 mg), in air atmosphere (60 ml/min). Further tests were performed by treating the fabrics in a muffle at 1100 °C for 1 h.

The flame retardancy properties of the prepared samples were measured through flammability and combustion tests. As already reported, such tests are complementary in order to entirely describe a realistic fire scenario (Alongi et al., 2011b).

The flammability test in vertical configuration was carried out by applying a propane flame for 5 s at the centre of a fabric specimen (50 mm × 100 mm) and repeating the application for at least two times: this configuration allows to test the fabrics in the most drastic way. The test was repeated 5 times for each formulation, measuring burning time and rate and the final residue as well. This test aims to mimic the procedure described in ISO15025 standard, commonly employed for the protective garments, although the specimen size used in this work is smaller (100 mm × 20 mm vs. 200 mm × 16 mm in ISO15025).

Cone calorimetry (Fire Testing Technology, FTT) was employed to investigate the combustion behaviour of fabric square samples (100 mm × 100 mm × 0.5 mm) under an irradiative heat flow of 35 kW/m² in horizontal configuration, following the procedure described elsewhere (Tata, Alongi, Carosio, & Frache, 2011). The fabrics were placed in a sample holder and maintained in the correct

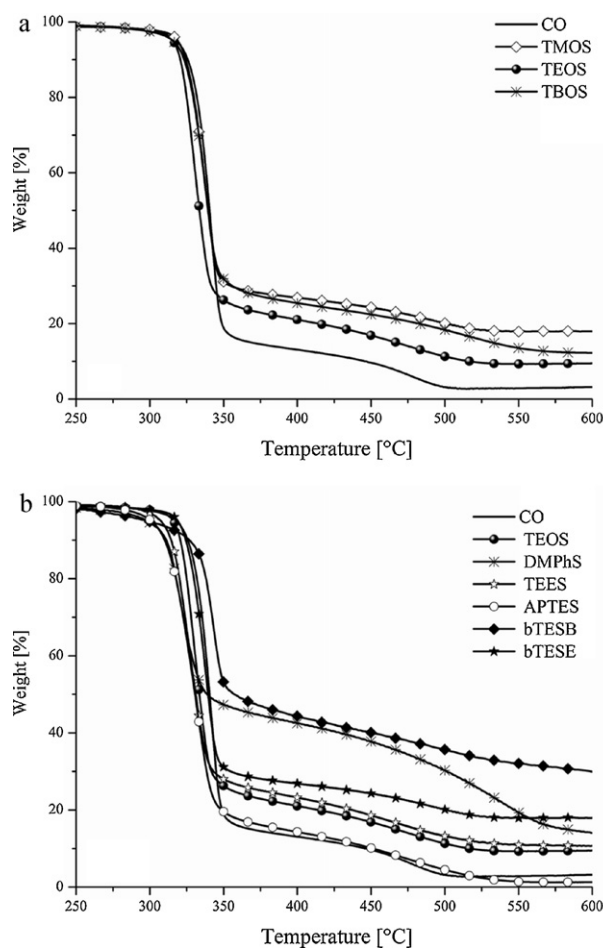


Fig. 1. TG curves of the fabrics in air.

configuration by a metallic grid. Time to ignition (TTI, s), total heat release (THR, kW/m²), heat release rate (HRR, kW/m²) and peak (pkHRR, kW/m²) and effective heat of combustion (EHC, MJ/kg) were measured. The fire performance index (FPI, s m²/kW) was also calculated as TTI to pkHRR ratio. The higher the FPI, the better is the flame retardancy performance (Schartel, Bartholmai, & Knoll, 2006). Total Smoke Release (TSR, m²/m²), Specific Extinction Area (SEA, m²/kg), carbon monoxide and dioxide yield ([carbon monoxide] and [carbon dioxide], kg/kg, respectively) were also evaluated. For each sample, the experiments were repeated four times in order to ensure reproducible and significant data. The experimental error was within 5%.

Since water can significantly influence the combustion behaviour of such a polar fabric as cotton, the water content was measured by using a Karl–Fisher titrator (Mettler Toledo, model V20). Fabric pieces (ca. 1 g) were heated up to 100 °C and the water content was established using a mixture of methanol, potassium metabisulphite and I₂ as titration system.

All Magic Angle Spinning (MAS) solid-state NMR spectra were acquired on a Bruker Advance III 500 spectrometer with a wide bore 11.7 Tesla magnet and operational frequencies for ²⁹Si of 99.35 MHz in HPDEC conditions. A 7 mm robe with MAS was employed in all the experiments. The samples were packed on a Zirconia rotor and spun at 5000 Hz.

The surface morphology of the treated samples was studied using a LEO-1450VP Scanning Electron Microscope, equipped with a X-ray probe (INCA Energy Oxford, Cu-K_α X-ray source,

Download English Version:

<https://daneshyari.com/en/article/10602283>

Download Persian Version:

<https://daneshyari.com/article/10602283>

[Daneshyari.com](https://daneshyari.com)