

# Thermal Properties and Combustion Behavior of POSS- and Bohemite-Finished Cotton Fabrics

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**ABSTRACT:** A finishing process with polyhedral oligomeric silsesquioxane (POSS) and bohemite nanoparticles has been exploited for enhancing the thermal stability and flame retardancy of cotton fabrics. The thermal behavior of flame retardant treated cellulosic fabric has been studied by thermogravimetric analyses (TGAs). It has been found that such nanoparticles favor the carbonization of the cellulose and slow down the kinetics of thermo-oxidation in air. At the same time, the finished fabrics have turned out to be more efficient with respect to neat cotton as far as the flame retardancy is concerned, pointing out an increase of the time to ignition (TTI) and a decrease of

the heat release rate (HRR). Furthermore, a comparison between the fire performances of the nanoparticles under study and a commercial phosphorus-based flame retardant has been investigated. The morphology and elemental composition present in the treated fabrics have been also investigated using scanning electron microscopy (SEM) coupled to the energy dispersive spectroscopy (EDS), and the results have been compared with the untreated fabric. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 426–436, 2012

**Key words:** flame retardancy; cotton; thermal properties; combustion behavior

## INTRODUCTION

Flame resistant fabrics for industrial and military uses represent one of the most important global markets of the textile world. To guarantee human safety, most of the textile materials are properly treated to become fire resistant, according to their final use in such application fields as protective garments, upholstery, furniture, mattresses, and bed-linen. There have been many researchers who have studied the mechanism of degradation of cellulose.<sup>1,2</sup> The pyrolysis of cellulose is a chain-unzipping degradation initiated by a heterolytic bond scission of glucose producing levoglucosan. The lability of the C-6 hydroxyl group in the cellulose repeating unit is crucial to depolymerization. So far, several retardant additives, such as phosphorus-based compounds, have been used to treat cotton textiles, and in some formulation, their efficiency could be further enhanced by addition of some nitrogen containing additives giving rise to the synergistic phosphorus–nitrogen action.<sup>3</sup> To produce flame retardant treatments with lower environ-

mental impact for textile fabrics, different approaches can be explored by means of nanotechnology. Indeed, as far as synthetic fibers (like polyamide 6 or polyester) are considered, it is possible to directly introduce different types of nanoparticles within the fibers by melt spinning,<sup>4–12</sup> whereas for natural substrates, the deposition of nanoparticles can be achieved by using the impregnation/exhaustion process (finishing) from aqueous suspensions. In the latter case, two different strategies, i.e., a bottom-up or a top-down approach, can be easily used.

By the bottom-up approach, it is possible to create singular nanoparticles or aggregates of different types through various synthetic strategies, whereas by the top-down approach, preformed nanoparticles are used in suspension. Our research group has just shown that sol–gel processes, which represent a bottom-up approach, can lead to the formation of *in situ* generated silica nanoparticles or silica coatings directly onto polyester, cotton, and their blends. By this way, it is possible to enhance the thermal stability and flame retardancy of polyester, cotton, and blends of them.<sup>13,14</sup>

On the other hand, the top-down approach, which exploits the availability of preformed nanoparticles, can be also useful to achieve the same purpose. Furthermore, the impregnation of nanoparticle suspension stable in water<sup>15,16</sup> or layer by layer assembly of nanoparticle layers has turned out to be promising and encouraging approaches to enhance the thermal

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stability and the flame retardancy of textile fabrics.<sup>17,18</sup>

To this aim, in the present work, two types of nanoparticles, a polyhedral oligomeric silsesquioxane (POSS) and an aluminum oxide hydroxide (bohemite) modified with sulfonate salts (OS1), have been investigated. POSS is characterized by a nanometric cage structure containing covalently bonded reactive functionalities suitable for polymerization or grafting. On combustion of such a polymer composite, POSS acts as a precursor forming thermally stable ceramic materials at high temperature.<sup>19</sup> Instead, bohemite nanoparticles could behave like an efficient flame retardant because of their endothermic decomposition accompanied by the release of water, resulting in cooling and dilution effects.<sup>20</sup>

Nowadays, limiting oxygen index (LOI) is the testing method commonly used in both industry and laboratory, although this procedure can only quantitatively determine the material ability to ignite and does not give any useful information about the burning behavior of polymers. In the literature, several papers on the flammability properties of both neat and treated cotton follow ASTM D 2863-70 standard and discuss data based on LOI determination.<sup>21-28</sup> As an alternative, some authors indicate the use of a different vertical test developed and set up by Mostashari et al.<sup>29-32</sup> (ASTM D1230-94). With the introduction of such a sophisticated calorimetric instrumentation for testing polymers as the cone calorimeter based on oxygen consumption, the measure of the main combustion parameters [time to ignition (TTI), total heat release and heat release rate (HRR), and corresponding peak] has become feasible<sup>7,10-16,33-36</sup>, thus allowing to complete the characterization of the combustion behavior for the textile substrates.

In an effort to develop novel environmentally friendly flame retardant, the present article reports and compares the performances of halogen-free finishes based on bohemite nanoparticles modified by sulfonate salts or on a POSS bearing eight *n*-propylammonium chloride groups, linked by different binders, onto cotton fabrics. Thermal stability and flame retardancy of the finished fabrics have been compared with that of the neat cotton by using thermogravimetric analysis (TGA) and cone calorimeter, whereas the morphology and surface composition of untreated and treated samples were examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis.

## EXPERIMENTAL

### Materials

The used plain-weave pure cotton fabric (214 g/m<sup>2</sup>), provided by Klopman International S.r.l. (Frosinone,

Italy), was previously pretreated in 2% nonionic detergent at 40°C for 20 min and treated in petroleum ether for 1 h. The scoured fabric was then rinsed thoroughly in tap water, dried in the open air, and kept in a desiccator with silica gel. The cleaned samples were conditioned under standard atmospheric pressure at 65 ± 2% relative humidity and 20 ± 1°C for at least 24 h prior to all experiments. A POSS cage molecule carrying eight *n*-propylammonium chloride groups or a bohemite modified by sulfonate salts (hereafter referred to as POSS and OS1 and generically identified as nanoparticles, (NPs), in tables and figures) were purchased from Hybrid Plastics Inc. (Hattiesburg, MS) and Sasol Chemical Europe Ltd. (Solihull, UK), respectively, and were used as received. Different types of binders (A–E reported in Table I) supplied by Europizzi S.p.A. (Bergamo, Italy) and Bozzetto S.p.A. (Bergamo, Italy) were used as received.

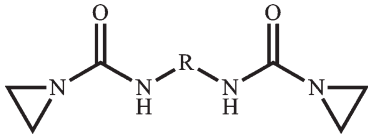
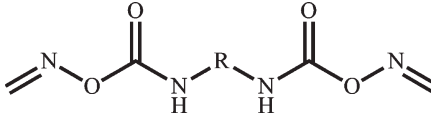
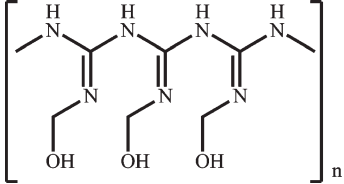
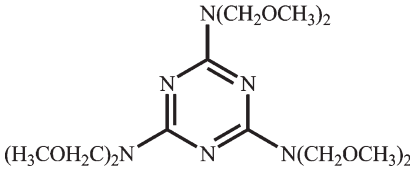
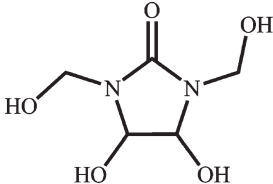
To compare the flame retardant properties of the formulations under study, a standard already flame retardant treated cotton (210 g/m<sup>2</sup>) was provided by Klopman International S.r.l. (Frosinone, Italy) and used as received. This product contains ca. 13 wt % of a phosphorus-based salt and hereafter is coded as cotton + flame retardant (FR).

### Preparation of cotton-binder-POSS and bohemite systems

Cotton fabrics were linked to POSS or bohemite systems using different agents that have functional groups able to react with hydroxyl groups of bohemite and ammonium groups of POSS, respectively. The first two binders, A and B, are bifunctional isocyanates blocked by ethylenimine and ketoxime, respectively. They consist of adducts containing a comparatively weak bond formed by the reaction between an isocyanate and a compound containing an active hydrogen atom. At elevated temperatures, the reaction tends to proceed in such a way as to regenerate the isocyanate and the blocking agent (Fig. 1).

The regenerated isocyanate groups are very reactive toward coreactants containing hydroxyl (or amine) functional groups, through an addition mechanism (Fig. 2). C–E compounds are formaldehyde-based binder agents. They have hydroxymethylene reactive groups that can form covalent bridges between cellulose and nanoparticles, as reported in Figure 3, where reactive groups of E connect cellulose and NPs. D binder shows the hydroxymethylene groups blocked by methanol: under slightly acidic conditions, a condensation reaction should occur among methoxy functional groups from hexamethoxymethylmelamine, cellulose hydroxyl groups, and nanoparticle hydroxyl/amine groups, to form covalent bonds joining cellulose-melamine-NPs (Fig. 4). Methanol was formed as a by-product of the reaction.

**TABLE I**  
Structure of the Binders Used to Treat Cotton

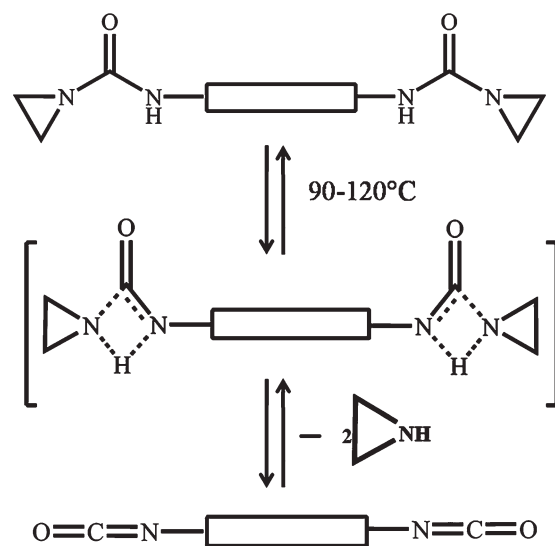
Code	Type binder	Trade name binder	Molecular formula
A	Blocked bifunctional isocyanates <sup>a</sup>	Cepolink PA	
B	Blocked bifunctional isocyanates <sup>a</sup>	Cepolink ICB	
C	Dicyanamide-formaldehyde polymer	Berfix FR	
D	Melamine-formaldehyde	Resin MF	
E	Dimethyloldihydroxyethyleneurea (DMDHEU)	Reacel BCF	

<sup>a</sup> R = alkyl chain.

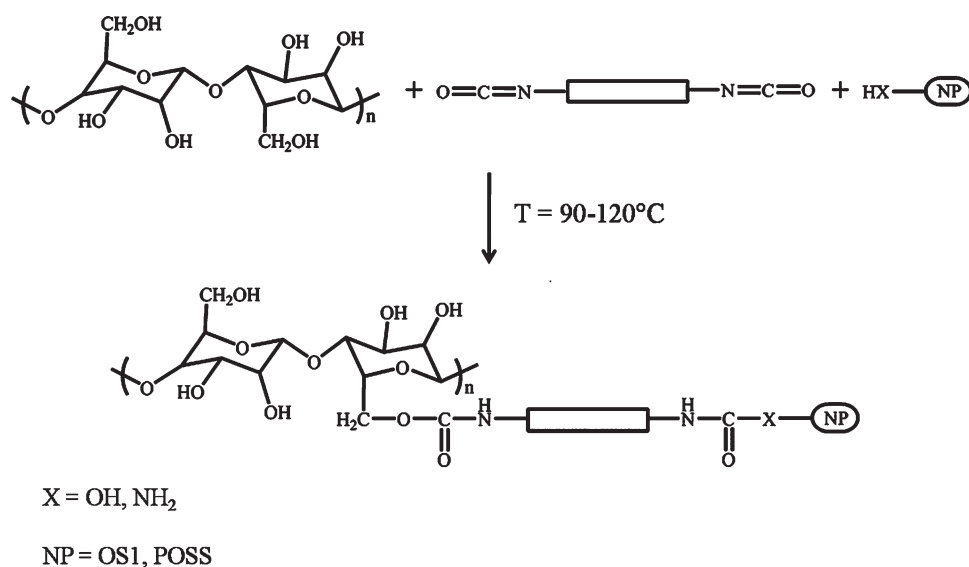
The amounts of NPs and binders employed are given in Table II. The nanoparticle amount was set at 1% owf (on weight fabric). The binder concentration was set at 1% owf for A–C and E, whereas D binder amounts used in the present study (3% owf) were those recommended by Europizzi for the one-pass conventional continuous process.

For D and E, a catalyst was required to start the polymerization reaction, namely dimethylbenzene sulfonic acid and magnesium chloride, respectively (as 20% of the binder weight). The mixtures of nanoparticles and binder were dispersed in a 100 mL aqueous bath through Ultra Turrax stirrer (IKA RW 16) for 1 min. The cotton samples (20 × 30 cm<sup>2</sup>) were dipped in the bath for 2 min and padded by a laboratory pad mangle (Werner Mathis, Zurich, Switzerland) with nip-pressure set to obtain 50% wet pick-up. The fabrics were dried and cured in a laboratory oven at the time and temperature required for the binder coupling reaction. In Table III, the formulation of all performed applications is shown. Each fabric is labeled by the codes of the corresponding nanoparticles and binders employed.

At least, two samples of cotton treated only with POSS and bohemite, and five treated only with each binder were prepared as reference samples following



**Figure 1** Deblocking scheme of blocked isocyanate heat-curable system.

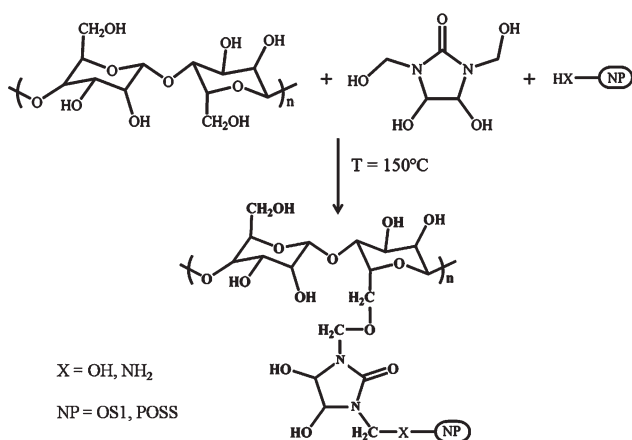


**Figure 2** Reaction scheme among reactive groups of isocyanates (A and B binders), cellulose, and NPs.

the procedure mentioned above. For POSS-based system, samples containing 2% and 5% of nanoparticle were prepared, as well. These samples were coded in Table VI as cotton + E + X%POSS, where  $X = 1, 2, \text{ or } 5$  owf %.

### Scanning electron microscopy

Observations were carried out using a Leica Electron Optics 435 VP SEM with an acceleration voltage of 15 kV and a 20 mm working distance. Specimens were mounted on aluminum stubs with double-sided adhesive tape. The metallization with gold was performed in rarefied argon atmosphere (20 Pa) using an Emitech K550 Sputter Coater, with a current of 20 mA for 180 s. The instrumentation was equipped with an INCA Energy Oxford X-ray probe (Cu- $K_{\alpha 1}$ ,  $k = 1.540562 \text{ \AA}$ ), useful to perform elemental analysis by EDS.



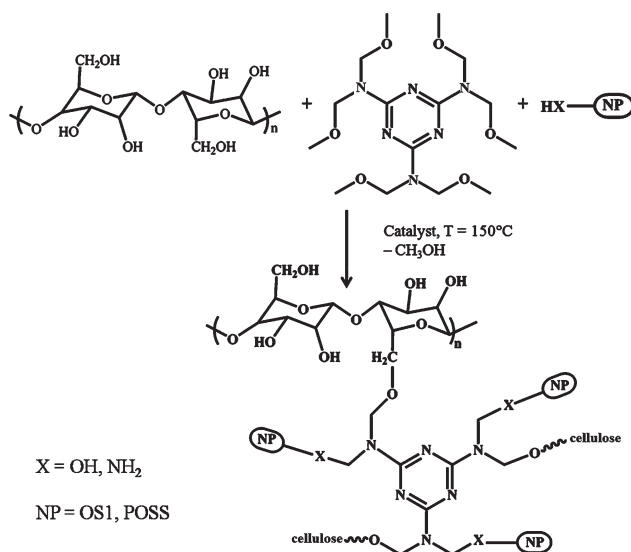
**Figure 3** Reaction scheme among reactive groups of E, cellulose, and NPs.

### Thermogravimetric analysis

A TA instruments Q500 thermobalance provided with a platinum pan was used. The measures were conducted in nitrogen or air atmosphere in the temperature range 50–800°C with a heating rate of 10°C/min. The experimental error was  $\pm 1\%$  by weight. The data collected were Tonset5% (5% weight loss),  $T_{\text{max1}}$  (maximum rate of weight loss; hereafter,  $T_{\text{max1}}$  and  $T_{\text{max2}}$  were referred to the two steps of degradation), and the residues at 500 and 800°C.

### Oxygen consumption calorimetry (cone calorimetry)

A cone calorimeter (fire testing technology, FTT) was used under a heat flux of 35 kW/m<sup>2</sup> according



**Figure 4** Reaction scheme among reactive groups of D, cellulose, and NPs.

**TABLE II**  
Concentrations of Applied Nanoparticles and Binders

Compound	% owf	g in 100 mL	pH	Cured time/ temperature (min/°C)
NPs	1	2	7	2/150
A	1	2	>7	3/90
B	1	2	7	3/150
C	1	2	5.5	20/40
D <sup>a</sup>	3	6	5	2/150
E <sup>a</sup>	1	2	5	2/150

<sup>a</sup> Catalyst added as 20% on resin weight.

to ISO 5660, following the procedure described elsewhere.<sup>36</sup> The parameters are TTI (s), HRR (kW/m<sup>2</sup> g), and the relative peak (pkHRR, kW/m<sup>2</sup> g). Fire performance index (FPI, sm<sup>2</sup> g/kW) was also calculated as ratio between TTI and pkHRR. For all formulations, the test was repeated three times, and the experimental error is ±5%.

### Limiting oxygen index

The flammability properties in terms of LOI value were measured by an oxygen index apparatus (FIRE) according to the ISO4589 standard.

## RESULTS AND DISCUSSION

### Morphology

Different binders were used to bond covalently OS1 and POSS to cotton fibers: morphological analyses performed by SEM showed the presence of the main components of the two fillers on the fiber surface. As far as bohemite is concerned, Figure 5 shows two magnifications of cotton treated with B as a binder and OS1 [Fig. 5(a,c)]: a homogeneous distribution and fine dispersion of the filler were found. The elemental analysis by EDS carried out on the whole sample area of the fabric [Fig. 5(a)] reveals the presence of C, O, and Al elements (Table IV), in the corresponding spectrum [Fig. 5(b)]. The amount of Cl element detected is presumably due to an impurity, namely the catalyst used to industrially produce the B binder. The mapping of the Al element

[Fig. 5(d)], a component of bohemite, results homogeneously distributed and finely dispersed at a nanometric level on sample. For the other binders, similar morphologies and elemental distribution were found.

On POSS, only the E binder was tested: as for bohemite, a homogeneous distribution [Fig. 6(a,b)] and a nanometric Si element dispersion [Fig. 6(c)] of POSS on cotton fibers have been detected.

### Thermal stability

The thermal and thermo-oxidative stability of the treated samples has been investigated by TGAs. As an example, the thermogravimetry (TG) and differential thermogravimetry (DTG) curves of the untreated cotton and of the fabrics treated with POSS, E binder, and E/POSS formulation have been reported in Figure 7(a,b), respectively.

It is evident that the degradation profile of cotton in air has been modified by the presence of the nanofillers, whereas that in nitrogen (data not given) did not show any clear differences. As is known, cotton cellulose usually decomposes in air by three steps, which are well described by Price et al.<sup>37</sup> The first step, located in the range 300–400°C, involves two competitive pathways which yield aliphatic char and volatile products; in the second step (between 400 and 800°C), some aliphatic char is converted into aromatic structures, yielding CO and CO<sub>2</sub> as a consequence of simultaneous carbonization and char oxidation. Finally, at ca. 800°C, the char and any remaining hydrocarbon species are further oxidized, mostly to CO and CO<sub>2</sub>. In our systems with nanoparticles, two peaks, which correspond to the first two steps (Table V) as reported by Price et al.,<sup>37</sup> are observed in the temperature range between 320 and 520°C, with the following differences as compared with the neat cotton behavior:

#### (A). Cotton-bohemite system

- (i). It can be seen that the beginning cotton degradation occurs at higher *T*s in presence of bohemite nanoparticles linked to cellulose moieties (except when binder C is used: Tonset5% of 274°C, the same as for

**TABLE III**  
Untreated and Treated Fabric Codes

NP	Treated fabrics					
—	Untreated cotton	Cotton + A	Cotton + B	Cotton + C	Cotton + D	Cotton + E
OS1	Cotton + OS1	Cotton + A + OS1	Cotton + B + OS1	Cotton + C + OS1	Cotton + D + OS1	Cotton + E + OS1
POSS	Cotton + POSS	—	—	—	—	Cotton + E + POSS

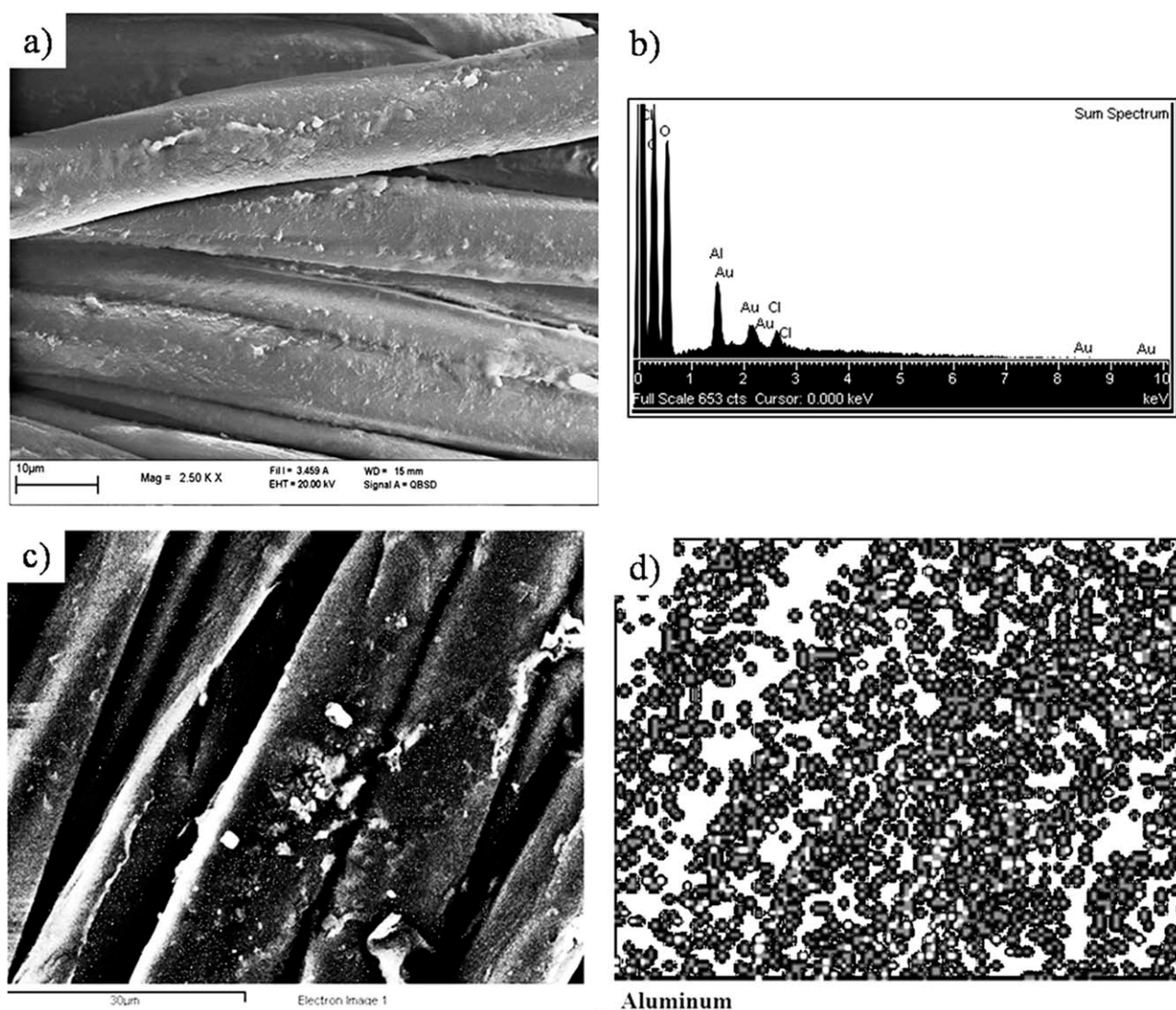


Figure 5 SEM micrograph (a), EDS analysis (b), and Al map (c and d) of cotton + B + OS1.

neat cotton). Cotton treated with bohemite simply adsorbed on its surface has a Tonset5% of 278°C, very close to the neat cotton value.

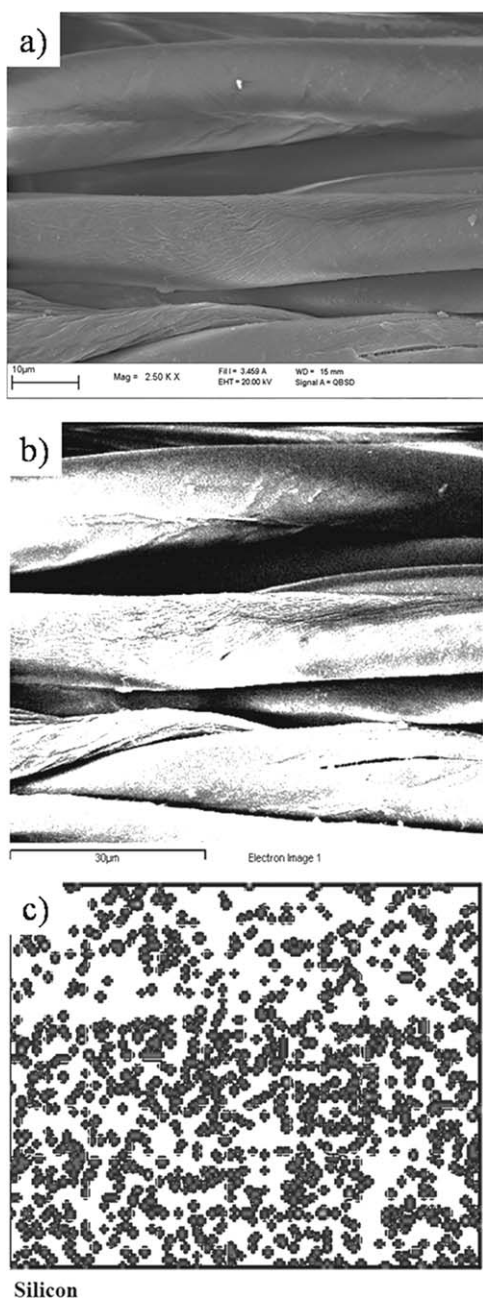
- (ii). Irrespective of this initial displacement, the first degradation step is steeper, as evidenced by the lower value of  $T_{\max 1}$ , as referred to  $T_{\max 1}$  value of 344°C for cotton. Differences between Tonset5% and  $T_{\max 1}$  are much lower than the value of  $\sim 70^\circ\text{C}$  for neat cotton, ranging from 39 to 52°C.
- (iii). On the contrary,  $T_{\max 2}$  is displaced to higher values, as compared with cotton, with larger differences  $T_{\max 2} - T_{\max 1}$ . This result underlines the slower rate of degradation kinetics in the second step.
- (iv). The residue at 500°C is two–three times higher for cotton/bohemite linked system than for neat cotton. This residue on the

surface of the samples acts as a physical barrier towards heat and oxygen transfer to the bulk polymer. Oxidation is achieved at higher temperatures leaving an appreciable residue also at 800°C, in contrast to

TABLE IV  
EDS Data of Cotton + B + OS1

Element	Weight (%)	Atomic (%)
C	39.90	48.39
O	54.72	49.84
Al	2.45	1.33
Cl	0.68	0.28
Au <sup>a</sup>	2.25	0.17
Total	100.00	—

<sup>a</sup> Au was used as conductive layer in SEM analysis as described in Experimental section.



**Figure 6** SEM micrograph (a) and Si map (b and c) of cotton + E + POSS.

neat cotton for which the residue is negligible.

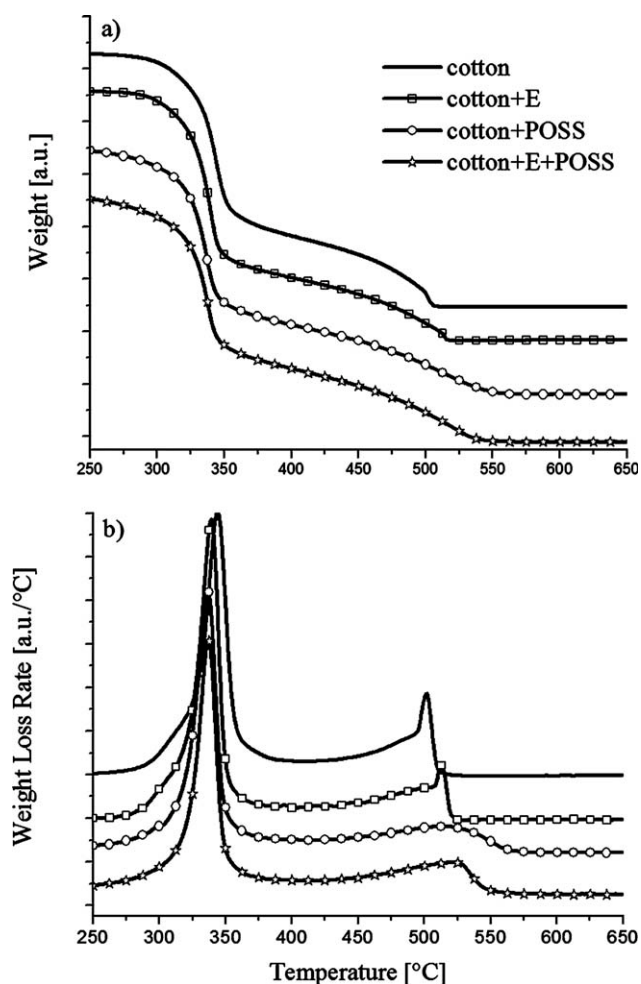
(B). Cotton-POSS system

- (i). Tonset5% is much lower than the value found for neat cotton and bohemite linked systems.  $T_{max1}$ , on the contrary, has a value which is almost the same as those of the other systems. The first degradation step, therefore, is rather slow for this system with the highest residue at 500°C (more than three times that of cotton). Differences between  $T_{max2}$  and  $T_{max1}$  remain quite large

and, again, the residue at 800°C is the highest found for the systems under study.

### Combustion behavior

The combustion data by cone calorimetry for untreated and treated cotton fabrics are summarized in Table VI and represented in Figure 8 as HRR curves. As far as the TTI is concerned, a general increase of it has been registered due to the presence of nanoparticles either only absorbed or covalently linked to the cotton fibers. As shown by the inset of Figure 8(a), where the curves in the range 0–30 s are given for bohemite-containing systems, the TTI increase is evident. Bohemite coupled to C binder and POSS with E binder [Fig. 8(b)] have been found to be the most promising systems to slow down the ignitability of cotton. Indeed, with these latter additives for finishing, the TTI of cotton reaches 22 s against 14 s of the neat sample. A possible explanation of this phenomenon is due to the chemical



**Figure 7** TG (a) and DTG (b) curves in air of cotton treated with POSS.

**TABLE V**  
TGA Data of Neat and Treated Fabrics in Air

Formulation	$T_{\text{onset5\%}}$ (°C)	$T_{\text{max1a}}$ (°C)	$T_{\text{max2a}}$ (°C)	Residue at 500°C (%)	Residue at 800°C (%)
Cotton	274	344	502	4	—
Cotton + OS1	278	339	502	9	1
Cotton + A	270	322	503	9	2
Cotton + A + OS1	285	331	513	8	2
Cotton + B	296	343	505	8	1
Cotton + B + OS1	297	336	502	8	2
Cotton + C	276	334	509	13	1
Cotton + C + OS1	274	326	511	13	2
Cotton + D	289	338	508	12	1
Cotton + D + OS1	289	331	508	12	2
Cotton + E	286	339	513	10	1
Cotton + E + OS1	283	331	507	10	2
Cotton + POSS	248	337	517	13	2
Cotton + E + POSS	248	337	523	13	3
Cotton + FR	275	347	505	16	3

<sup>a</sup> From derivative TG curves.

composition of the nanoparticles under study. Indeed, bohemite is an aluminum oxide hydroxide,  $\gamma$ -AlO(OH), that dehydrates in the range of 100–300°C, releasing water and subsequently transforming into the crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase at ~ 420°C.<sup>38</sup> In this manner, during the first degradation step of cotton, the volatile products generated by the cellulose under irradiation are diluted, and the ignition is reached after a longer time as compared with neat cotton. Furthermore, the ceramic barrier due to the presence of just formed alumina inhibits the further combustion of the cotton. Analogously, the systems containing POSS create onto the textile surface a silica-based barrier able to physically protect the

polymer from the heat and the oxygen. The above barriers turn out to be responsible of the remarkable decrease of both HRR and the corresponding peak. Referring to bohemite, the best binder has been found to be D: for this system the decrease of pkHRR achieves ca. 40% of the reference value for neat cotton. Almost the same strong decrease has been found for POSS covalently linked to cotton by E binder.

To define the best performances in terms of flame retardancy, the FPI has been also calculated for all samples: in general, treated samples are characterized by a higher FPI (>0.43 sm<sup>2</sup> g/kW) than neat cotton (0.24 sm<sup>2</sup> g/kW). Comparing all the collected

**TABLE VI**  
Cone Calorimetry Data and LOI Values of Neat and Treated Fabrics

Formulation	TTI (s)	pkHHR (kW/m <sup>2</sup> g)	$\Delta$ pkHHR (%)	FPI (sm <sup>2</sup> g/kW)	LOI (%)
Cotton	14	57	-	0.24	19
Cotton + FR	7	35	-40	0.20	31
NP = OS1 <sup>a</sup>					
Cotton + OS1	22	50	-12	0.44	19
Cotton + A	18	38	-33	0.47	19
Cotton + A + OS1	22	41	-28	0.54	20
Cotton + B	20	37	-35	0.54	19
Cotton + B + OS1	20	45	-18	0.44	19
Cotton + C	17	42	-26	0.41	19
Cotton + C + OS1	20	36	-37	0.56	20
Cotton + D	20	39	-32	0.51	20
Cotton + D + OS1	21	35	-39	0.60	20
Cotton + E	16	43	-25	0.37	19
Cotton + E + OS1	20	46	-19	0.43	19
NP = POSS					
Cotton + POSS	18	35	-39	0.51	20
Cotton + E + 1%POSS	22	34	-40	0.65	20
Cotton + E + 2%POSS	34	30	-30	1.13	21
Cotton + E + 5%POSS	26	30	-30	0.87	21

<sup>a</sup> OS1 amount is 1% owf.



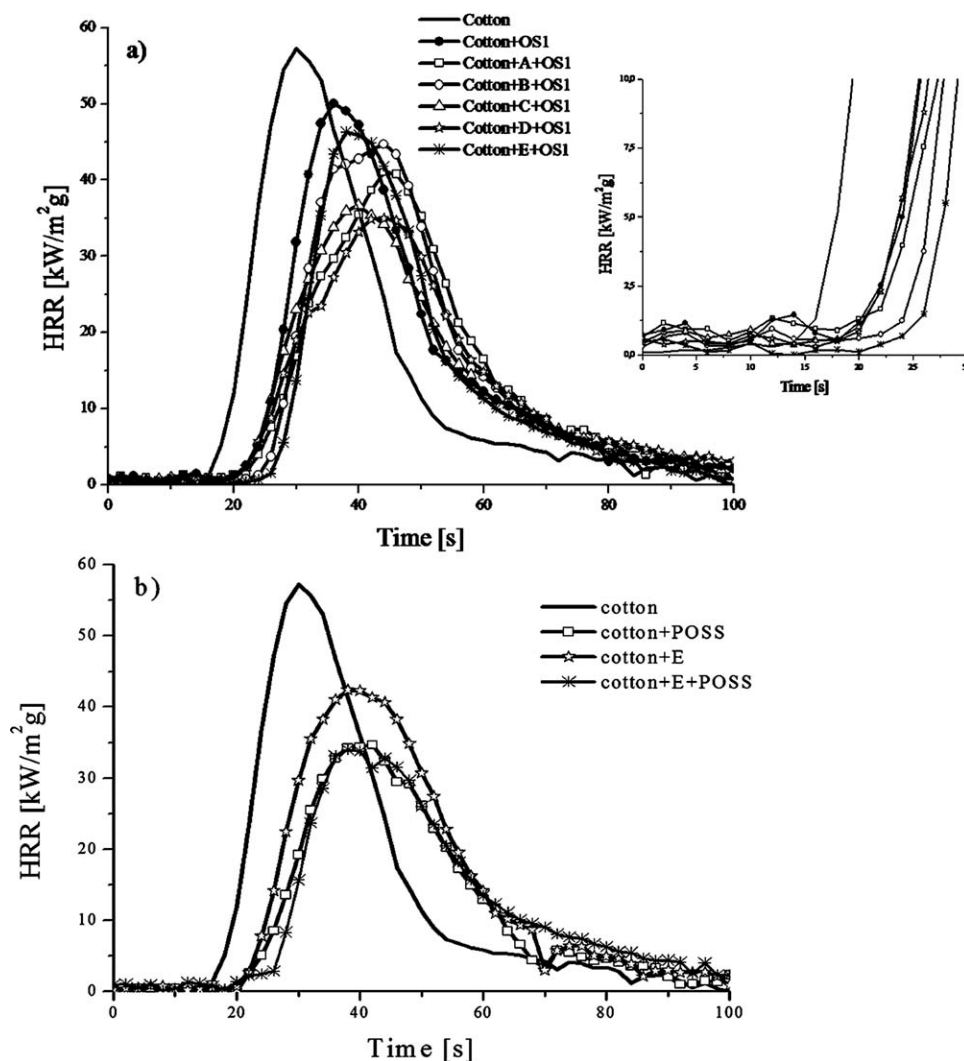


Figure 8 HRR curves of cotton fabrics treated with bohemite (a) and POSS (b).

data (Table VI), the best performances of the cotton have been achieved using POSS with E binder (FPI =  $0.65 \text{ m}^2 \text{ g/kW}$ ). For this system, the role of nanoparticle amount has been investigated, as well. As shown in Table VI, increasing POSS concentration, the flame retardancy properties of cotton increase, since the TTI surprisingly increases, and, consequently, the FPI. This latter result is very significant, since, as it is well known in the literature, nanoparticles usually influence in negative way the ignition by TTI decrease. However, this improvement reaches the maximum value (FPI =  $1.13 \text{ m}^2 \text{ g/kW}$ ) when the employed POSS amount is 2 wt % showing that a limit maximum of concentration exists due to the organization of POSS molecules on fabrics.

#### Nanoparticles versus phosphorus-based flame retardant

To evaluate the real efficiency of the systems containing the nanoparticles under study, a comparison

between their performances and those of a common flame retardant for the cotton has been investigated on the flammability and combustion point of view. The behavior of the phosphorus-based flame retardant and nanoparticles employed in the present article is diametrically opposite in these two tests, because the heat reaches the cotton in different ways, namely, through the direct application of a flame (LOI test) or by an irradiative flux (cone calorimetry test). The flammability of the prepared samples has been evaluated by LOI tests, in which a flame of methane is applied directly to the specimen, whereas the combustion behavior has been investigated by a heat flux of  $35 \text{ kW/m}^2$  produced by a conical source.

The registered LOI values are collected in Table VI. Regardless of the nanoparticle type, when the concentration is 1 wt %, both bohemite and POSS are not able to increase LOI value in significant way in comparison with neat polymer: indeed, LOI of the treated fabrics remains 19–20%. Referring only to

POSS, when the amount of this nanoparticle is increased, a slight improvement has been registered. Nevertheless, these results are not comparable with those obtained when a phosphorus-based flame retardant is used: indeed, for the latter system, LOI value reaches 31%. As it is well known, the higher the LOI value, the better is the flame retardancy performance.

The collected data show that the used flame retardant is able to act chemically with the polymer in condensed phase, favoring its carbonization. This phenomenon is due to the formation of phosphoric and polyphosphoric acid at high temperatures that are able to modify the combustion mechanism of the cellulose. In this manner, a carbonaceous residue, able to protect the textile, is formed on its surface, when a flame is applied. This result is also confirmed by TGAs, as it is observable in Table V, comparing the residues at 500°C. Analogously, the nanoparticles are able to induce the carbonization of cellulose, but through a physical mechanism due to the formation of a ceramic barrier on the textile surface. Nevertheless, their efficiency is lower than that of the flame retardant under study.

As far as the combustion behavior is considered, the best performances have been registered for the systems containing nanoparticles (both bohemite and POSS), irrespective of their concentration onto the fabric, as it is evident comparing the FPI values in Table VI. The flame retardant, acting as described above, is able to decrease the heat release and corresponding rate of cotton combustion, such as the nanoparticles: indeed, the  $pkHRR$  is reduced of 40%, as well as for Cotton + E + 1%POSS. However, it is also responsible of the ignition anticipation ( $-9$  s), and consequently its performances (in terms of FPI value) are lower than those of POSS-finished textiles. In this contest, nanoparticles turn out to be better flame retardant than phosphorus-based additive, since they have a different action mechanism. At high temperatures, under an irradiative flux, nanoparticles form a ceramic barrier on the textile surface (alumina or silica for bohemite or POSS-based systems, respectively) that acts physically as thermal insulator. This barrier protects the underlying polymer from the oxygen and heat, limiting the further polymer combustion. In this manner, the cellulose ignition is delayed. On the contrary, the phosphorus-based flame retardant favors the polymer carbonization and, in this way, reduces the total heat release and the corresponding rate, but it is not able to protect it during the first step of degradation/ignition.

## CONCLUSIONS

In the present work, cotton has been linked, using different binders, to a bohemite modified by sulfo-

nate salts or a POSS carrying eight *n*-propylammonium chloride groups. It has been shown by electron microscopy and elemental analysis (coupled to mapping of the main components) that these nanoparticles are homogeneously distributed on the surface of cotton fibers and finely dispersed at nanometric level. Furthermore, the nanoparticles have turned out to play a protective role on the thermo-oxidation of the cotton, modifying its degradation profile. Indeed, they have enhanced the thermal stability of cotton in air favoring the mechanism of carbonization and, thus, increasing the final residue at high temperatures, slowing down the overall thermo-oxidation kinetics. The main result is the formation of a carbonaceous surface char that acts as a physical barrier toward the heat and oxygen transfer to the polymer. By the cone calorimetry data, it is possible to conclusively affirm that the kinetics of cotton combustion process has been modified by nanoparticles treatment as compared with that of neat cotton: the TTI increases and the HRR decreases up to 40%.

The flame retardancy properties of the nanoparticle-finished fabrics have been compared with those obtained using a phosphorus-based flame retardant in terms of LOI tests and cone calorimetry measurements. It is found that the performances of nanoparticles are higher than those of the flame retardant used in this paper, only during the combustion tests by cone calorimetry. This finding is due to the tendency of these nanoparticles to release water at high temperatures and form a ceramic barrier able to delay the cellulose ignition and reduce the heat release and corresponding rate.

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