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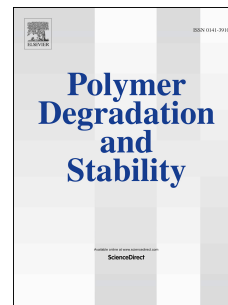
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1 **Synthesis and characterization of a phosphorous/nitrogen based sol-gel coating as a novel**  
2 **halogen- and formaldehyde- free flame retardant finishing for cotton fabric**

3

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16

17 **Abstract**

18 A novel formaldehyde- and halogen-free coating, containing phosphorus, nitrogen and silicon, was  
19 synthesized with a promising approach to enhance flame retardancy of cotton fabric. To this aim, a  
20 new sol-gel precursor, comprising in the same molecule P, N and Si, namely (3-  
21 Glycidyloxypropyl)triethoxysilane modified N-(phosphonomethyl) iminodiacetic acid (PGPTES),  
22 was co-hydrolysed and co-condensated with tetraethylorthosilicate (TEOS), as silane linker, and  
23 used for producing a self-extinguishing cotton fabric coating. The structure of PGPTES was  
24 characterized by <sup>1</sup>H/<sup>13</sup>C/<sup>31</sup>P nuclear magnetic resonance and the obtained coating was investigated  
25 by FT-Infrared Spectroscopy and Scanning Electron Microscopy. The thermal properties of the  
26 treated fabric were studied by Thermogravimetric Analyses and Cone Calorimetry Tests. The

27 obtained results show that the synthesized coating is able to catalyse the dehydration and char  
28 formation of cellulose based polymer at a lower temperature, thanks to the thermal decomposition  
29 of phosphate giving rise to acidic intermediates, able to further react with cellulose-based fabric,  
30 hence improving the flame retardant properties of the latter.

31

32 Keywords: Sol-gel; GPTES; N-(Phosphonomethyl)iminodiacetic acid; Textile finishing; flame  
33 retardancy.

34

### 35 **1. Introduction**

36 Recently, nanotechnology has become a fast-growing area of research in the textile field because of  
37 its many potential applications allowing the development and evolution of a new class of improved  
38 materials [1]. Advanced applications have been developing through textile or textile-based  
39 materials, such as nanofibers, as well as nanocomposite fibres [2]. Meanwhile, nanoparticles are  
40 also successfully being used in conventional textiles to impart new functionalities and improved  
41 performance [3, 4]. In fact, they have high surface energy and a large surface area-to-volume ratio,  
42 which makes them easy to be linked to the treated substrate, increasing the durability of the  
43 functions imparted to textile materials [5]. Currently, one of the biggest scientific and technological  
44 challenges is the design of new materials in order to develop innovative applications. In this  
45 context, the role of preparative chemistry is to provide the compounds useful for obtaining  
46 innovative materials: among them, hybrids exploit the peculiarities of both the organic and the  
47 inorganic chemistries, hence giving rise to an almost unlimited number of applications. As an  
48 alternative to chemistry employed for the surface modification, a range of solution techniques have  
49 emerged, including co-precipitation, hydrothermal processing, solvothermal methods and sol-gel  
50 chemistry [6]. Among these, the sol-gel approach shows some particular advantages, being centred  
51 on the ability to produce a solid-state material from a chemically homogeneous precursor. The  
52 "Design" of sol-gel materials - and their material properties - is to some extent possible by changing

53 the chemical composition and arrangement of the molecular building blocks and by deliberately  
54 tailoring their nano- and micro-structure. The sol-gel technique, consisting in hydrolysis and  
55 condensation reactions, is based on hydrolysable precursors-building blocks - mostly metal or semi-  
56 metal alkoxides (precursors); among them, the most widely studied are silicon alkoxides,  
57 characterized by the strong covalent Si-O bonding and a hydrophobic behaviour that makes them  
58 immiscible with polar media. In textile applications, the most representative precursors are  
59 organofunctional trialkoxysilanes ( $R'-Si(OR)_3$ ), because of their unique structure bearing three  
60 polymerizable groups, which enables the formation of a highly oriented polymer network structure  
61 with an incorporated organic moiety.

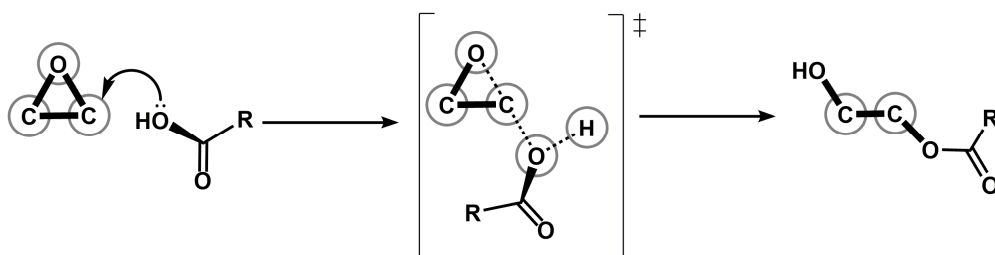
62 The sol-gel process represents a simple method for the development of a coating with selected  
63 protective properties, presenting many advantages, such as the possibility to achieve an  
64 environmentally-friendly surface functionalization of substrates and the easy adaptation of this  
65 finishing process to the existing processing lines in industrial scale production [10–13]. Depending  
66 on the chemical structure of the network-modifying moiety, different functional properties can be  
67 tailored on the material surface. Among these, it is worthy to mention antimicrobial [14], UV  
68 radiation protection [15,16], biomolecule immobilization [17], dye fastness [16,18], anti-wrinkle  
69 finishing [19] and super-hydrophobicity [20], as well as antistatic properties, odour control, stimuli-  
70 responsive performance [21] and strength enhancements [22]. In addition, since silica coatings exert  
71 a thermal shielding effect on polymer surfaces improving the flame retardancy of the treated fabrics  
72 [23], the use of sol-gel methods for conferring flame retardant properties to textile fabrics, in  
73 particular cellulose-based fibres, has been documented by several research groups [24]. In fact,  
74 cotton, thanks to its peculiarities such as strength, durability, flexibility and air permeability, as well  
75 as good biocompatibility, low cost and good mechanical properties [25], is one of the most  
76 important materials employed not only for producing apparel but also home furnishings and  
77 industrial products, namely medical supplies, industrial thread and tarpaulins [26]. Unfortunately,  
78 this cellulosic material has a low limiting oxygen index (LOI) and combustion temperature that

79 makes it highly flammable [27]. In order to meet fire safety regulations and expand the use of  
80 cotton in textile applications that require flame resistance, a significant number of flame retardant  
81 treatments has been developed in the last century [28], among which formaldehyde-based and  
82 halogenated compounds have been the most employed. Although they show high performance with  
83 excellent washing fastness, in most of them, the presence of active hydroxymethyl units causes the  
84 release of formaldehyde from the treated fabrics both during the fabric application and throughout  
85 the lifetime of the garment, which is not environmentally compatible [29]. For what concerns  
86 halogenated compounds, recently, research studies regarding their persistence, ability to bio-  
87 accumulate, and potential for toxicity have led to increasing restrictions and regulations on the  
88 production and use of some of them. In particular, such compounds as polybrominated biphenyls,  
89 penta and octobromodiphenylethers have been banned, as they could generate corrosive and toxic  
90 combustion products (e.g. dioxins and furans). [30]. Given the negative impact of formaldehyde and  
91 bromine-based finishes on human health, since they are carcinogenic and bio-accumulative,  
92 respectively, it is a primary focus for public safety to develop equivalent compounds, without  
93 formaldehyde and halogens. Replacing the above-mentioned flame retardants finishes with  
94 environmentally-friendly compounds represents an ecological step forward, in agreement with IPPC  
95 European Directive [31]. Phosphorus-based flame retardants seem to be a valid alternative for the  
96 above-mentioned FRs: in fact, unlike the halogen-containing compounds, which generate toxic  
97 gases, corrosive smoke, or harmful substances [30], they act in condensed phase, by converting into  
98 phosphoric acid or metaphosphoric acid during combustion or thermal degradation. Thus, non-  
99 volatile polyphosphoric acids can react with the decomposing polymer by esterification and  
100 dehydration to promote the formation of protective char [32]. The development of the latter provide  
101 lower flammability to fabric by protecting the underlying polymer from attack by oxygen and  
102 radiant heat. Besides, it was found that organophosphorus containing active nitrogen have  
103 multifunctional advantages and show higher effectiveness if compared with pure phosphorus  
104 counterparts: a) low toxicity during combustion, b) high efficiency measured by cone calorimeter,

105 and c) low smoke development in fire accidents [6]. Some nitrogen-containing compounds seem to  
106 accelerate phosphorylation of cellulose through the formation of a phosphorus-nitrogen polymeric  
107 species, and thus synergize the flame retardant action of phosphorus. The reason could be attributed  
108 to the type of bond between elements: P-N bonds are more polar than the already present P-O  
109 bonds, and the enhanced electrophilicity of the phosphorus atom increases its ability to  
110 phosphorylate the C(6) primary hydroxyl group of cellulose. By this way, the intra- molecular C(6)-  
111 C(1) rearrangement reaction forming levoglucosan is blocked. Meanwhile, the auto-crosslinking of  
112 cellulose promotes and consolidates the char formation derived by the action of the same flame  
113 retardants [33,34]. In addition to the above-mentioned compounds, silicon is demonstrated to be  
114 used as a flame-retardant element because it is able to produce a continuous layer of silica that  
115 retards char oxidation.

116 In this paper, we take advantage of the synergistic effect between silica and phosphorous in  
117 conferring flame retardant properties: in fact, the concurrent presence of P and Si elements in the  
118 same precursor can be exploited for preparing a hybrid coating that behave, at the same time, as a  
119 char promoter (with the same above-mentioned mechanism) and thermal shield, due to the metal-  
120 oxide ceramic network [35–40].

121 In this study, (3-Glycidyloxypropyl)triethoxysilane (GPTES), one of the most used silica precursors  
122 for hybrid silica-based textile finishing, was chosen since its ethoxysilyl groups and the reactive  
123 epoxy group allow promoting the adhesion with the treated textile surface and the reaction with  
124 other organic molecules, respectively. Furthermore, the epoxy ring can be simultaneously  
125 crosslinked, via extended covalent bonds, to form poly- or oligo-(ethylene oxide) derivatives, thus  
126 allowing the grow-up of a hybrid polyoxyethylene 3D-network. Carboxylic moieties of N-  
127 (phosphonomethyl) iminodiacetic acid (PMIDA), a nitrogen-containing carboxyphosphonate, react  
128 with GPTES epoxy groups to form a  $\beta$ -hydroxy propyl ester, following the mechanism proposed in  
129 Fig 1.



130  
131 **Fig. 1.** Proposed mechanism of reaction between PMIDA and GPTES.  
132

133 Combining the advantages of a facile synthesis with the use of a traditional application procedure,  
134 the proposed phosphorus-functionalized sol-gel precursor (PGPTES) emerges as promising  
135 candidate for next-generation of hybrid finishes based on the concurrent presence of Si, P and N,  
136 with breakthrough performances. Considering that PGPTES possesses both an inorganic moiety and  
137 a high phosphorus content, it is potential for serving as a facile, ~~eco-friendly~~ and efficient flame  
138 retardant agent for cellulosic fibres. Furthermore, the mild reaction conditions of the process make  
139 it very favourable for the deposition of a hybrid organic-inorganic coating during the finishing of  
140 cotton fabrics. In this research, the structure and surface morphology of the untreated and treated  
141 cotton fabric were investigated in detail by NMR and FT-IR spectroscopy and Scanning Electron  
142 Microscopy (SEM), equipped with an energy dispersive X-ray spectroscopy (EDX). Then, the  
143 surface chemical composition was investigated by X-ray Photoelectron Spectroscopy (XPS).  
144 Thermogravimetric analysis (TGA), cone calorimetry (CC), horizontal and vertical flame spread  
145 tests were exploited for evaluating the combustion behaviour, the thermal stability, as well as the  
146 flammability of the treated cotton samples.

## 147 148 **2 Experimental part**

### 149 150 *2.1. Materials*

151  
152 (3-Glycidyloxypropyl)triethoxysilane (GPTES, namely:  $\text{Si}(\text{OC}_2\text{H}_5)_3\text{C}_3\text{H}_5\text{O}_2$ ,  $\geq 98\%$ ) and

153 Tetraethoxysilane (TEOS, namely:  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\geq 98\%$ ) as sol-gel precursors, as well as N-  
154 (Phosphonomethyl)iminodiacetic acid hydrate (PMIDA, 97%, MW 227.11), monoethanolamine  
155 (MEA), and HCl (all reagent grades) were purchased from Sigma Aldrich (Italy) and used without  
156 any further purification. Scoured and bleached plain-weave cotton fabrics, with an areal density of  
157  $237 \text{ g/m}^2$ , were supplied by Mascioni Spa, Varese, Italy. In order to remove impurities that would  
158 scatter on the fabric surface randomly during manufacturing, before sol-gel treatments, all the  
159 fabrics were carefully cleaned by washing in a 2% non-ionic detergent (Tergipal NRZ, linear  
160 alcohol ethoxylate, kindly supplied by FTR SpA, Italy) at  $40 \text{ }^\circ\text{C}$  for 20 min, then rinsed several  
161 times with de-ionized water, and finally dried. Before all experiments, all the samples were placed  
162 under standard laboratory conditions ( $65(\pm 4)\%$  relative humidity and  $20(\pm 2) \text{ }^\circ\text{C}$  temperature) for 24  
163 h.

164

## 165 *2.2 Nanosol preparation and application process*

166

167 Pre-reacted precursor sol was initially prepared from a mixture of high purity GPTES and PMIDA.  
168 To promote the reaction between the epoxy group and the hydroxyl groups of the phosphonate, the  
169 reaction was carried out in the absence of water, with the goal of limiting the possibility that the  
170 epoxy group can either undergo hydrolysis to form the corresponding diol or polyaddition reactions  
171 and polyether linkages. Therefore, 10 g of PMIDA powder, finely grinded, were slowly added to 20  
172 ml of a TEOS/GPTES mixture (precursors molar ratio 25:75) into a 100 ml flask. The mixture was  
173 kept for 2 h at room temperature, under vigorous stirring, until the solution became clear. Finally, in  
174 order to start stepwise hydrolysis and condensation of oligomeric intermediate, 18.5 ml of water  
175 were added. Monoethanolamine (MEA) was used for adjusting the pH to 3 and to increase the  
176 nitrogen content of the FR system. The so-obtained solution was stirred for 3 h to complete the  
177 hydrolysis of both precursors. With the aim to produce the xerogel and investigate its chemical

178 structure, small amounts of the obtained sol were applied on glass slides, the solvent was removed  
179 at 80°C for 1 h and the thin film was then cured at 170°C for 1 h.

180 The cotton fabrics (20 cm x 30 cm) were dipped in the hybrid sol and then passed through a two-  
181 roll laboratory padding machine at nip pressure of 3 bar with about 75% of wet pick-up. After  
182 drying at 90°C for 5 min, the fabric sample was cured at 170°C in a laboratory oven for 5 min. The  
183 treated cotton sample was coded as CO\_T. The amount of coating deposited, calculated as add-on  
184 on the untreated sample ( $A$ , wt% owf), was calculated weighing the sample before ( $W_0$ ) and after  
185 the padding-curing treatment ( $W_1$ ), using a Mettler balance ( $10^{-4}$  g):

$$186 \quad A = \frac{W_1 - W_0}{W_0} \times 100 \quad \text{Eq. 1}$$

187 The value obtained from Eq. 1 represents the average of five independent replicates, with the  
188 standard deviation always lower than  $\pm 2\%$ .

189

### 190 2.3 Characterization

191

192 FTIR spectra of treated and untreated cotton samples were recorded using a Thermo Avatar 370  
193 spectrophotometer equipped with an attenuated total reflectance (ATR) device for solids analysis.

194 Spectra were analysed using Omnic 7.3 software. Fabrics were stored at room temperature for 48 h

195 in a stabilized atmosphere at 20°C and 60% RH. The analysis was performed with the samples  
196 placed onto a diamond crystal, within 4000 and 650  $\text{cm}^{-1}$ , with 64 scans and a resolution of 4  $\text{cm}^{-1}$ .

197 The collected spectra were normalized to the 1314  $\text{cm}^{-1}$  band, associated with the C-H bending  
198 mode of cellulose. Since infrared absorption bands of the silica-based coating applied onto the

199 fabric surface are covered by the strong vibrational peaks of cellulose, FTIR analysis was carried  
200 out also on pure xerogel in order to characterize it, thereby avoiding other influences. In addition,

201 based on the intensity and shift of vibrational bands of FTIR spectra, the treated sample was

202 compared with pristine cotton in order to assess the presence of the coating. The morphologies of

203 treated and untreated cotton fabrics, including the char residues after horizontal flame spread tests,  
204 were observed using scanning electron microscopy (LEO-1450VP, with beam voltage fixed at 5  
205 kV), equipped with an X-ray probe (INCA Energy Oxford, Cu-Ka X-ray source,  $k_{\alpha} = 1.540562 \text{ \AA}$ ),  
206 which was utilized for performing elemental analysis. Thermogravimetric analyses (TGA) were  
207 carried out on a TAQ500 apparatus, using a heating rate of  $20^{\circ}\text{C}/\text{min}$  in nitrogen and air  
208 atmosphere (gas flow:  $60 \text{ mL}/\text{min}$  for both the atmospheres). The experimental error was  $\pm 0.5\%$  on  
209 the weight and  $\pm 1^{\circ}\text{C}$  on the temperature. Combustion tests of square fabric samples ( $50 \text{ mm} \times 50$   
210  $\text{mm} \times 0.5 \text{ mm}$ ) were carried out on a Fire Testing Technology Ltd Cone Calorimeter, under  
211 ventilated conditions, using a  $35 \text{ kW}/\text{m}^2$  irradiative heat flow in horizontal configuration. The  
212 experiments were repeated four times for each material investigated to ensure reproducible and  
213 significant data; the experimental error was within  $3\%$ . The following parameters were registered:  
214 time to ignition (TTI, s), peak of heat release rate (pkHRR,  $\text{kW}/\text{m}^2$ ), total heat release (THR,  
215 assessed at the end of the test,  $\text{MJ}/\text{m}^2$ ), ratio of carbon dioxide and carbon monoxide yields, and  
216 final residue (%). The accuracy was up to  $3$  and  $10\%$  for CO and  $\text{CO}_2$  yields, respectively. A Fire  
217 Performance Index (FPI,  $\%/s$ ) was also calculated as final residue to TTI ratio and employed as an  
218 evaluating parameter: the higher the FPI value, the better the flammability performance.

219 The flammability of the cotton samples in the presence of a flame spread was measured both in  
220 horizontal and vertical configurations.

221 In the first case, the flame was applied on the short side of the specimen ( $50 \text{ mm}$ ) for  $10 \text{ s}$  and then  
222 removed rapidly. Two horizontal marks were drawn on the specimens (at  $25$  and  $75 \text{ mm}$  from the  
223 side, on which the flame was applied) and the time ( $t_1$  and  $t_2$ ) required to the flame to reach them  
224 was measured. Besides, other relevant parameters, such as total burning time and final residue, were  
225 evaluated. Alternatively, when the test was performed in vertical configuration, a methane flame  
226 was applied for  $5 \text{ s}$  at the bottom of a fabric specimen ( $50 \text{ mm} \times 100 \text{ mm}$ ), repeating the test  $3$  times  
227 for each formulation in order to get reproducible data. A Flammability Performance Index (FPI,  
228  $\%/s$ ) was also calculated as the ratio of final residue to the total burning time and used as an

229 evaluation parameter: the higher the FPI values, the better is the flame retardancy performance.  
230 Prior to flammability and combustion tests, all the specimens were conditioned at  $23\pm 1$  °C for 48 h  
231 at 50% R.H. in a climatic chamber.

232  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded in  $\text{D}_2\text{O}$  solutions or in a  $\text{CD}_3\text{OD}/\text{D}_2\text{O}$   
233 mixture (1:1=v/v) at 500, 125 and 202 MHz, respectively; coupling constants ( $J$ ) are given in hertz,  
234 and the attributions are supported by heteronuclear single-quantum and multi-bond coherence  
235 (HSQC-HMBC) and correlation spectroscopy (COSY) experiments; all proton NMR experiments  
236 were run with a water suppression pulse sequence.

237 XPS measurements were performed by using a ESCALAB MkII spectrometer equipped with a non-  
238 monochromatized Al  $\text{K}\alpha$  source and a five channeltrons detection system. The samples were fixed  
239 to the holder by metallic clip. The spectra were collected at 40 eV pass energy and the binding  
240 energy scale was calibrated positioning the C 1s peak from adventitious carbon at  $\text{BE} = 285.0$  eV.  
241 All data were collected and processed by Avantage v.5 software.

242

### 243 **3. Results and Discussion**

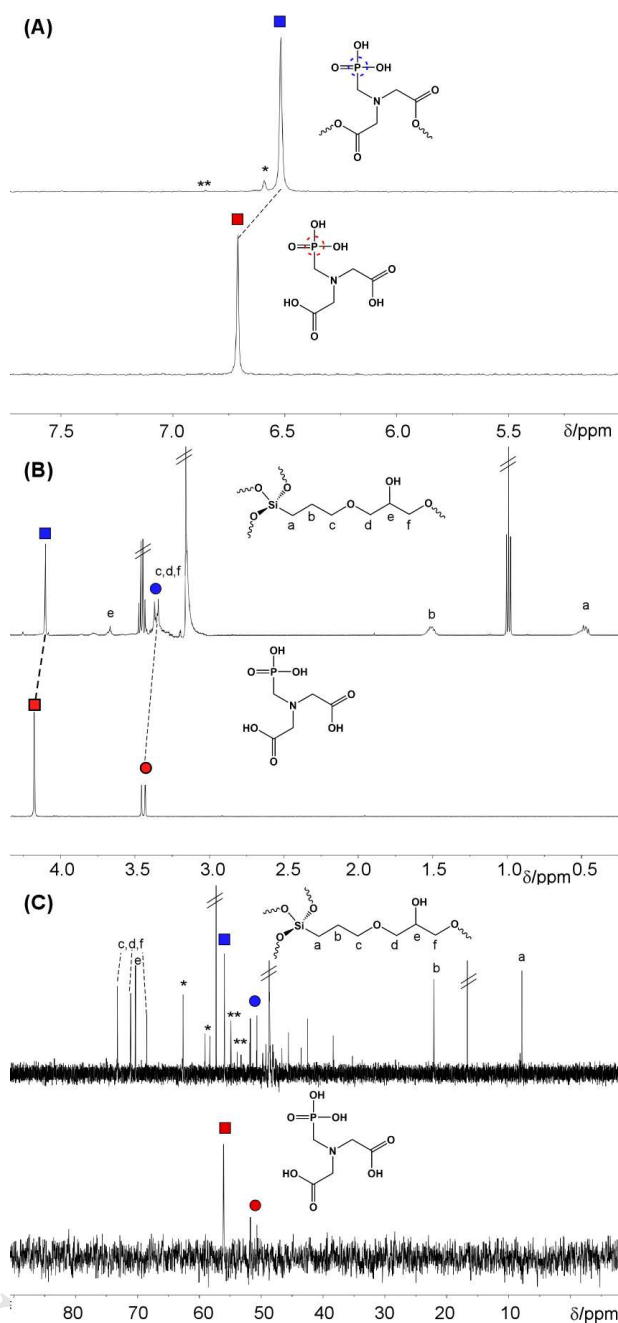
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#### 245 *3.1 NMR characterization and structure determination*

246

247 The PGPTES xerogel film, covering a glass-slide, was carefully removed, chopped and suspended  
248 in a  $\text{CD}_3\text{OD}/\text{D}_2\text{O}$  mixture (1:1=v/v), in order to characterize the silylated derivative by means of  
249 homonuclear and heteronuclear  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR, mono- and bidimensional NMR  
250 spectroscopy. Figure 2 shows the recorded  $^{31}\text{P}\{^1\text{H}\}$ ,  $^1\text{H}$ , and  $^{13}\text{C}\{^1\text{H}\}$  NMR stacked plots,  
251 respectively, in comparison with the starting PMIDA molecule (on the bottom of the figures, in  
252  $\text{D}_2\text{O}$ ) and the suspended xerogel coating TEOS\_GPTES\_PMIDA (PGPTES), in a 1/1  $\text{CD}_3\text{OD}/\text{D}_2\text{O}$   
253 mixture.

254



255

256 **Fig. 2.** Stacked NMR spectra relative to a solution of starting PMIDA molecule in  $\text{D}_2\text{O}$  (bottom)257 and a suspension of PGPTES xerogel (top) in a  $\text{CD}_3\text{OD}/\text{D}_2\text{O}$  (1:1=v/v) mixture as solvent at 298 K:258 **A.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz); **B.**  $^1\text{H}$  NMR, with the main proton assignment; (500 MHz); **C.**259  $^{13}\text{C}\{^1\text{H}\}$  NMR, with the main carbon assignment (125 MHz).

260

261 The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra in Figure 2A clearly shows the expected lower frequency shift of the  $^{31}\text{P}$ 262 signal relative to the PMIDA molecule from  $\delta = 6.71$  (red square) to 6.52 ppm (blue square),

263 evidencing that a more shielding environment is enclosing the  $^{31}\text{P}$  nucleus of the PMIDA; after the  
264 reaction with GPTES. Two minor  $^{31}\text{P}$  containing species are present in solution at very slight  
265 concentration (highlighted in Figure 2A with a star and double stars).

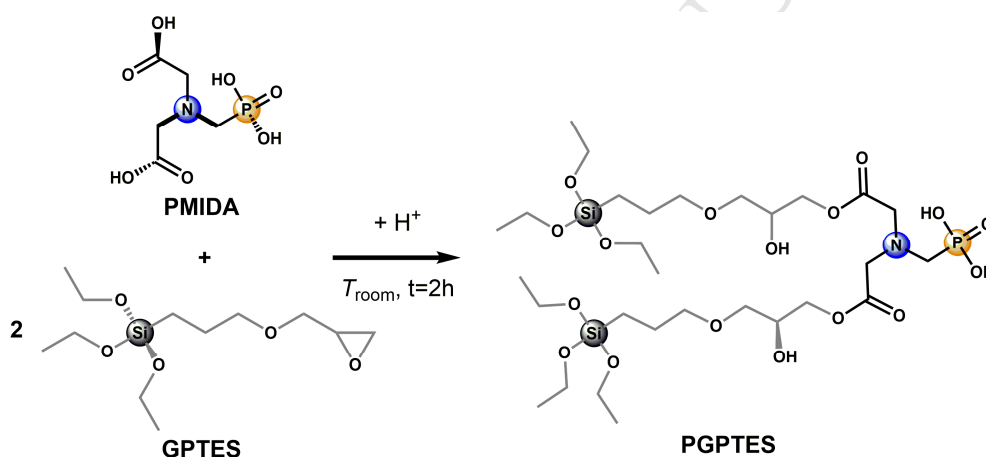
266 In agreement, the aliphatic regions of the  $^1\text{H}$  NMR spectra in figure 2B clearly show: (i) the  
267 corresponding upfield proton shifts for the two methylene groups  $\text{CH}_2\text{-COOH}$  and  $\text{CH}_2\text{-P}$ , that shift  
268 from  $\delta = 4.17$  and  $3.44$  (m,  $^2J_{\text{PH}}=12.3\text{Hz}$ ) ppm, to  $\delta = 4.10$  and  $3.36$  (m,  $^1J_{\text{PH}}=12.5\text{Hz}$ ) ppm,  
269 respectively (red square and circle vs blue square and circle); (ii) the presence of the expected  
270 protonic pattern for the GPTES open ring derivative, bringing a hydroxyl and an ester group bonded  
271 to two vicinal carbon  $\text{C}_e$  and  $\text{C}_f$  atoms ( $\delta = 0.47$ ,  $\text{CH}_{2a}$ ;  $1.51$ ,  $\text{CH}_{2b}$ ;  $3.36$ ,  $\text{CH}_{2c}+\text{CH}_{2d}+\text{CH}_{2f}$ ;  $3.66$   
272  $\text{CH}_{2e}$ ), in a 2:1 concentration ratio with respect to protons belonging to the PMIDA molecule [41–  
273 43]; (iii) the presence of the methylene and the methyl proton resonances relative to free ethanol  
274 moieties.

275 Similar results can be drawn with the assignments of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, shown in figure  
276 2C, that undoubtedly display: (i) the presence of the pattern expected for the PMIDA\_GPTES  
277 fragments, characterized by almost the same  $^{13}\text{C}$  chemical shift for the carboxylic group and for the  
278 two methylene  $\text{CH}_2\text{-COOH}$  and  $\text{CH}_2\text{-P}$ , as well as the starting PMIDA molecule (i.e.  $\delta = 168.6$ ;  
279  $55.9$ ,  $^3J_{\text{PC}} = 3.4$  Hz;  $51.3$  ppm,  $^1J_{\text{PC}}=136$  Hz vs  $\delta = 168.4$ ;  $56.1$ ,  $^3J_{\text{PC}} = 2.6$  Hz;  $51.2$  ppm,  $^1J_{\text{PC}}=135$   
280 Hz, respectively); (ii) diol, dioxane and polyethyleneoxide silylated functionalities (not assigned  
281 peaks) embedded in the final xerogel matrix [43], together with other minor phosphorous  
282 containing PMIDA derivatives (star and double stars).

283 All these findings confirm that the GPTES epoxy ring opening reaction has successfully taken  
284 place, combined with the complete hydrolysis of the alkoxysilane end group. Even if solvent effects  
285 (due to a 50%  $\text{CD}_3\text{OD}$  presence as solvent for the PGPTES spectra) should be taken into account  
286 especially in the  $^1\text{H}$  spectra assignments, the high and already well-known nucleophilic substitution  
287 reactivity of the carboxylic groups towards the epoxy rings [42,44] led us to conclude that, in the  
288 final xerogel, the PMIDA molecule is mainly bonded firmly and covalently through two ester bonds

289 to the sol-gel based 3D matrix [45,46]; minor species may be assigned most probably to the  
 290 monosubstituted ester species or to the fully substituted species through the two acetic groups and  
 291 the phosphorous end. As previously shown, the epoxy ring opening of GPTES gives rise to the  
 292 formation of diol and silylated dioxane/polyether (PEO), through several hydrolysis and  
 293 polymerization reaction steps [43].

294 According to the reported results, a scheme of the occurred reaction is presented in Fig. 3 showing  
 295 the formation of a N-(Phosphonomethyl)imino diacetate hydroxy polysiloxane derivative through a  
 296 starting 1:2 molecular species, namely N-(Phosphonomethyl)imino bis{2-hydroxy-3-[3-  
 297 (triethoxysilane)propoxy]propyl acetate}}.



298  
 299 **Fig. 3** Scheme of the reaction occurring between PMIDA and GPTES

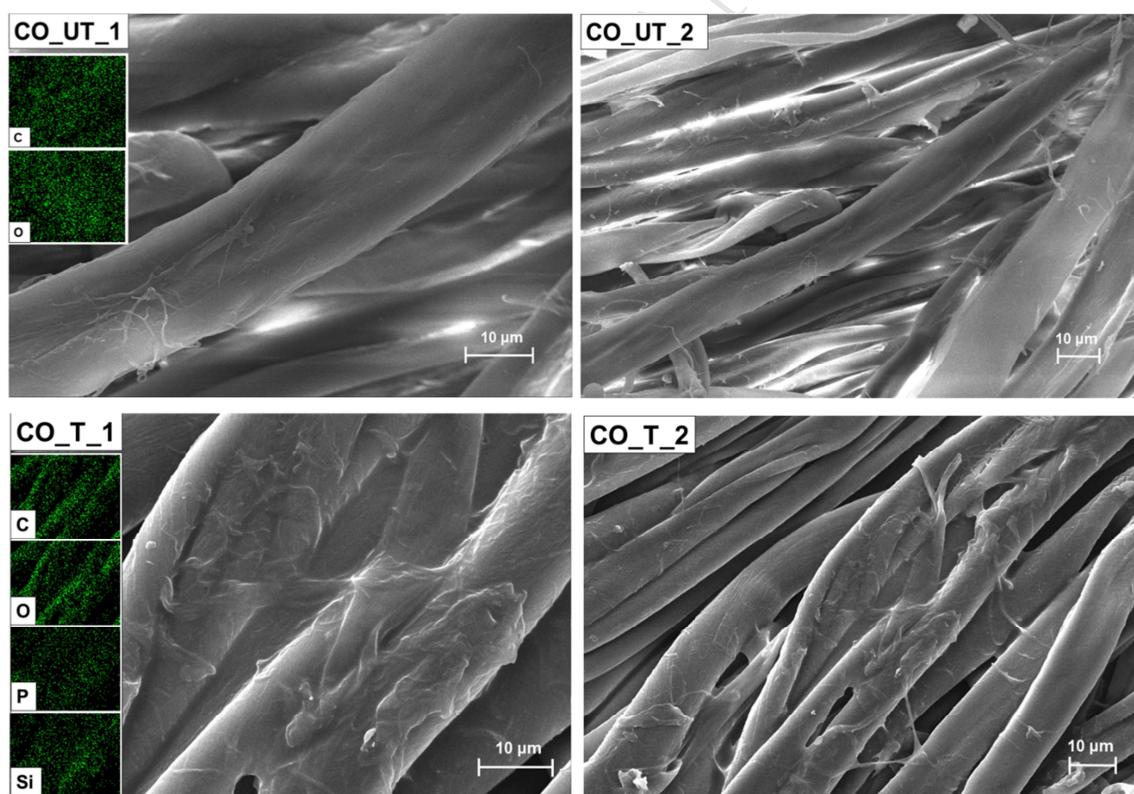
300

### 301 3.2 SEM-EDX analysis

302

303 Scanning electron microscopy was utilized to investigate the morphological features of untreated  
 304 and coated cotton fabrics. Fig. 4 shows SEM micrographs of cotton and the related EDX spectra  
 305 before and after hybrid sol-treatment. The latter results in 25.2% add-on, calculated according to  
 306 equation 1. In both magnifications, images of the untreated cotton sample show a flat assembly with  
 307 a twisted ribbon-like structure caused by spiralling of cellulose fibrils. The surface appears clearly  
 308 smooth with its veined natural morphology. After treatment, fibres are homogeneously covered by

309 the hybrid coating, showing free gaps between the warp and weft threads that maintain the same  
310 aspect of the control cotton fabric, suggesting that the sol-gel coating on the treated sample is very  
311 thin. Furthermore, semi-quantitative EDX investigation, employing a high beam voltage (i.e. 20  
312 kV), confirms the key information concerning the element composition of samples. With the aim of  
313 assessing the homogeneous distribution of coatings, five repeated measurements were carried out  
314 on different parts of each cotton sample. Although the maps reported in the images are qualitative,  
315 in the treated samples only phosphorus and silicon are present, along with carbon and oxygen  
316 shown in the control fabric, since the technique cannot detect nitrogen atom. Furthermore, the data  
317 listed in Tab. 1 show very similar results in all repeated tests, confirming a uniform presence of the  
318 above-mentioned elements on the treated fabric sample.  
319



320  
321 **Fig. 4.** SEM images of untreated (CO\_UT) and treated (CO\_T) cotton samples, at different  
322 magnifications, coded as \_1, \_2, for x2.50 K, x1.00 K, respectively.  
323  
324

325

326

327 **Table 1.**

328 Results (wt.%) of EDX analysis of untreated and treated samples.

Sample		C [%]	O [%]	P [%]	Si [%]
CO_UT	Unburned	46.10±0.07	53.9 ± 0.50	/	/
	Burned*	/	/	/	/
CO_T	Unburned	44.19±0.03	49.32±0.73	2.63±0.58	3.86±0.87
	Burned	60.53±1.33	30.01±0.54	5.9±1.51	4.23±0.06

329 \* no residue was collected after flammability test.

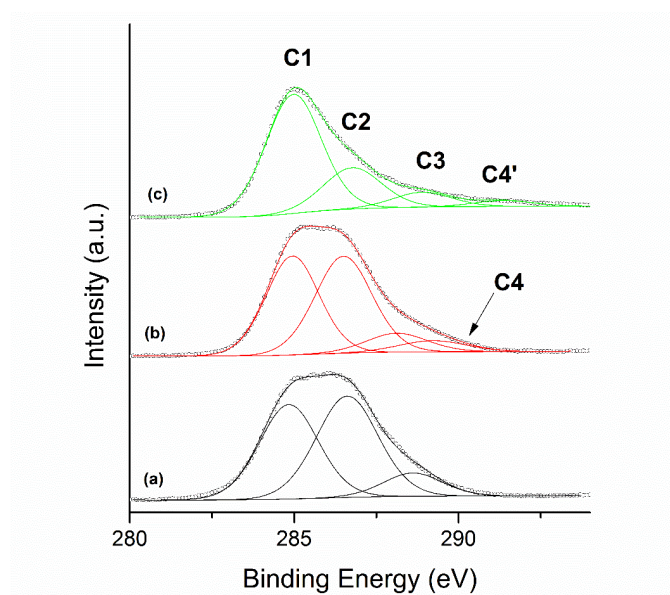
330

331 *3.3 XPS analysis*

332

333 In order to investigate the surface chemical composition of both coated and untreated cotton fabrics,  
334 the samples were investigated by XPS analysis. The presence of C and O was registered on both  
335 samples, while the coated sample also showed the presence of Si, P and N. The shape of the C 1s  
336 signal (Fig. 5(a)) was characteristic for cotton fabric, characterized by three peaks positioned at BE  
337 = 285.0 eV, 286.7 eV and 288.5 eV, with intensity ratio 1 : 1.1 : 0.2, and assigned to C–C/C–H, C–  
338 OH and C=O bonds, respectively. The sol-gel coating slightly modified the shape of C 1s signal  
339 (Fig. 5(b)), because it was very thin. However, the formation of the sol-gel coating was confirmed  
340 by the presence of Si, P and N. After flammability tests, the shape of C 1s signal significantly  
341 changed (Fig. 5(c)), where the intensity ratio of the peaks became 1 : 0.3 : 0.1 and a fourth peak was  
342 positioned at BE = 291.4 eV, due to the presence of carbonates. This changing was not unexpected,  
343 because it is typically for residual char samples [47]. Comparing the XPS quantitative analysis,  
344 shown in Tab. 2, it can be noted that sol-gel coating was partially decomposed during the  
345 flammability test, with a decrease of the atomic concentration of Si and an accumulation of P and C

346 elements on the outermost layers of the substrate. These last results may appear inconsistent with  
 347 those obtained by EDX analysis (Table 1). This is due to the different depth of each analysis. In  
 348 fact, XPS technique investigates the first layer of the sample (< 10 nm), while information depth of  
 349 EDX is approximately 1  $\mu\text{m}$ . Furthermore, the results are comparable (e.g. Si/P ratio) even if they  
 350 are given in wt% (EDX) and in at. % (XPS).  
 351



352  
 353 **Fig. 5.** Comparison of C 1s spectra of (a) untreated cotton fabric (CO\_UT), (b) treated cotton fabric  
 354 (CO\_T) and (c) carbonaceous char (CO\_C).

355

356 **Table 2.**

357 Surface chemical composition of the untreated cotton fabric (CO\_UT), treated cotton fabric (CO\_T)  
 358 and carbonaceous char (CO\_C).

	C (%)					N (%)	O (%)	P (%)	Si (%)
	C1: C-C/C-H	C2: C-OH	C3: C=O	C4: -COOH	C4': CO <sub>3</sub> <sup>-</sup>	NR <sub>3</sub>	-OH	Phosphate	SiOR
<b>BE (eV)</b>	285.0	286.6	288.1	289.2	291.4	400.5	532.8	133.7	103.3
<b>CO_UT</b>	29.1	32.7	7.2				31.0		
<b>CO_T</b>	26.4	27.6	5.8	3.7		2.3	29.1	1.7	3.5

CO_C	42.3	15.4	5.6	2.2	3.7	24.3	4.6	2.1
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359

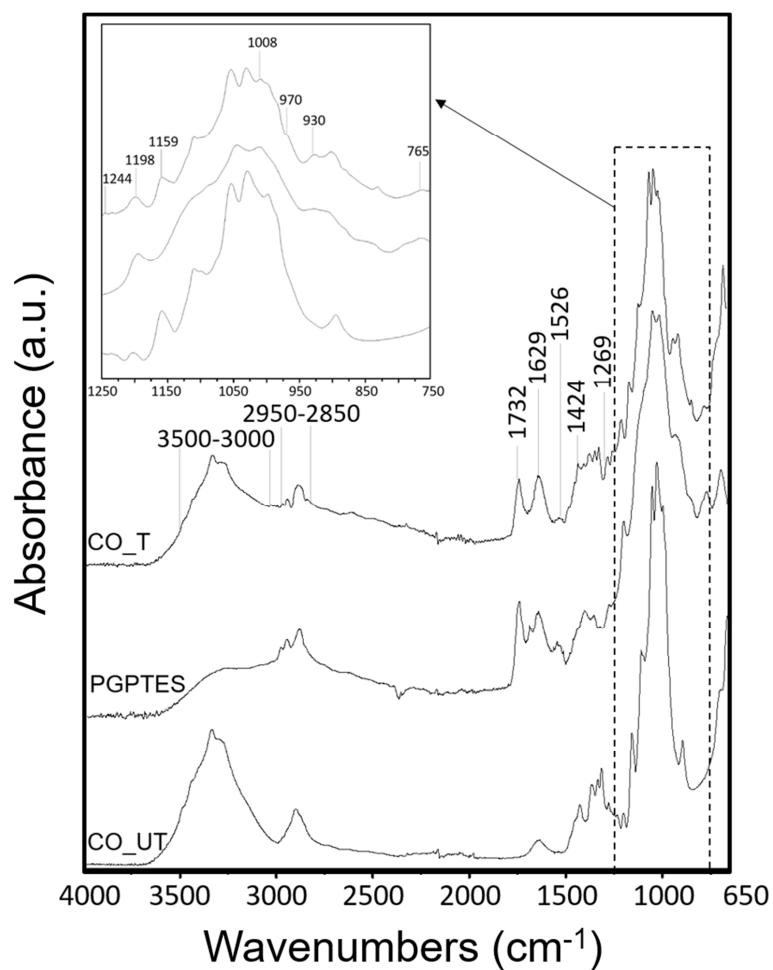
360 **3.4 ATR-FTIR spectroscopy**

361

362 The ATR-FTIR spectra of the untreated, treated cotton fabrics and pure xerogel prepared on glass  
363 slides, are compared in Fig. 6 and the most important bands are collected in Table 3. The analytical  
364 measurement of modified GPTES hybrid sol has been carried out, since the strong vibrational bands  
365 of the pure substrate could hide the characteristic peaks of the thin film applied onto the fabric  
366 surface. Comparing the xerogel spectrum with that of PMIDA, it can be highlighted the absence of  
367 a broad band at 2650-2450  $\text{cm}^{-1}$ , characteristic of such type of compounds and attributed to P-OH  
368 stretching vibration. Also the band at 929  $\text{cm}^{-1}$ , typical of P-OH bending signal, disappears. These  
369 findings, combined with the shift of the stretching vibration of P=O from 1215  $\text{cm}^{-1}$  to higher  
370 wavenumbers (1267  $\text{cm}^{-1}$ ), demonstrate an effective interaction between phosphorous compound  
371 and silica matrix. The other characteristic peaks that can be seen from xerogel spectrum are located  
372 at 1736  $\text{cm}^{-1}$  (stretching vibration of ester carbonyl), at 1635  $\text{cm}^{-1}$  and 1540-1520  $\text{cm}^{-1}$  (typical of  
373 the absorption of  $\text{NH}_2$  group). The region between 1200 and 750  $\text{cm}^{-1}$  includes peaks characteristics  
374 of silicon matrix: 1194  $\text{cm}^{-1}$  (Si-O-Si asymmetric stretching), 1045  $\text{cm}^{-1}$  (Si-O-Si), 1009  $\text{cm}^{-1}$  (Si-O  
375 stretching), 907-930  $\text{cm}^{-1}$  (Si-OH stretching), 763-790  $\text{cm}^{-1}$  (Si-O-Si symmetric stretching).  
376 Moreover, the opening of the epoxide ring was observed through the absence of its characteristic  
377 infrared bands at 1255  $\text{cm}^{-1}$  (ring breathing), 907  $\text{cm}^{-1}$  (asymmetric ring deformation) and 851  
378  $\text{cm}^{-1}$  (symmetric ring deformation) [46, 48]. FTIR spectroscopy was also carried out in order to  
379 confirm the successful reaction between the hybrid coating and cotton. As shown in Figure 5, the  
380 spectrum of untreated cotton exhibits O-H stretching absorption between 3500 and 3000  $\text{cm}^{-1}$ , C-H  
381 stretching absorption around 2950-2850  $\text{cm}^{-1}$ , and C-O-C stretching absorption around 1160  $\text{cm}^{-1}$ .  
382 These bands are consistent with those of the typical cellulose backbone. The spectrum of the coated  
383 cotton appears quite similar to that of the untreated one. With respect to the latter, an overall slight

384 decrease of the intensities of characteristic hydrogen-bonded OH stretching vibrations is observed:  
385 this finding may be attributed to the interaction of the coating with the cotton functional groups. In  
386 the treated cotton sample, some new characteristic peaks appear, such as the broad absorption band  
387 in the region 2970-2850, which is attributed to the introduction of the  $-CH_2$  group; these peaks are  
388 proportional to the quantity of carbon included in the grafted molecules and, in particular, the band  
389 of asymmetric stretching vibration of the methylene group located at  $2925-2970\text{ cm}^{-1}$  and a band  
390 attributable to symmetric stretching vibration at  $2850-2920\text{ cm}^{-1}$  can be detected. The absorption  
391 band at  $1732\text{ cm}^{-1}$  was assigned to the stretching vibration of carbonyl of ester group [49]. The  
392 majority of the peaks typical of  $-PO_3$  moiety are hidden by intense cellulose bands; the only one that  
393 is clearly visible is at  $1269\text{ cm}^{-1}$ , assigned to the  $P=O$  stretching vibration. The most important  
394 peaks attributable to the sol-gel coating were identified at 1008, 930 and  $765\text{ cm}^{-1}$  assigned to Si-O-  
395 Si asymmetric stretching, Si-OH stretching, and Si-O-Si symmetric stretching, respectively. The  
396 peak expected to be at about  $1040\text{ cm}^{-1}$  is overlapped with a broad band between 1050 and  $1014$   
397  $\text{cm}^{-1}$  attributed to the characteristic peaks of cellulose. Some changing in the intensity of IR bands  
398 appearing onto the treated textile fabric in the range between  $1240$  and  $1160\text{ cm}^{-1}$  are assigned to  
399 Si-O-C bonds, thus confirming the reaction between the hydrolysed silane precursor and the  
400 cellulosic substrate. Although these peaks may be considered weak, they are of great importance  
401 because they are a proof of the interaction between the substrate and the precursor [50].  
402 Furthermore, the presence of amino group from MEA is observed at about  $1629$  and  $1526\text{ cm}^{-1}$  due  
403 to symmetric and asymmetric N-H bending modes, respectively.

404



405

406 **Fig. 6.** AT-FT IR of hybrid coating onto glass slide (PGPTES), untreated (CO\_UT) and treated  
 407 cotton (CO\_T) samples.

408

409 **Table 3**

410 Major vibrational frequencies of the sol-gel based films.

Experimental wavenumbers (cm <sup>-1</sup> )		Literature wavenumbers	Vibrational mode
Glass substrate	Fabric substrate	(cm <sup>-1</sup> )	
3300	3500–3000	3500–3000	v (O-H)
		[51]	
2850	2950–2850	2980–2800	v (C-H)
		[51]	

1736	1732	1735	v (C=O)
		[52]	
1635, 1540-1520	1629, 1526	1600, 1575	v (N-H)
		[53]	
–	1424	1429	$\omega$ (C-H)
		[51]	
1266	1269	1267	v P=O
		[54]	
–	1244	1240	Si-O-C
		[55]	
1194	1198	1200	$v_{as}$ (Si-O-Si)
		[51]	
–	1159	1160	$v_{as}$ C-O-C
		[51]	
1009	1008	1001	v (Si-O-Si)
		[51]	
907-930	930	952	v (Si-OH)
		[51]	
790-763	765	749–786	$v_s$ (Si-O-Si)
		[51]	

411

412 **3.5 Thermal behaviour**

413 The thermal and thermo-oxidative stability of the untreated and sol-gel treated cotton fabrics has  
 414 been assessed by thermogravimetric analyses performed in nitrogen and air, respectively.

415 The TG and dTG thermograms of sol-gel treated and untreated cotton samples are shown in Fig. 7;

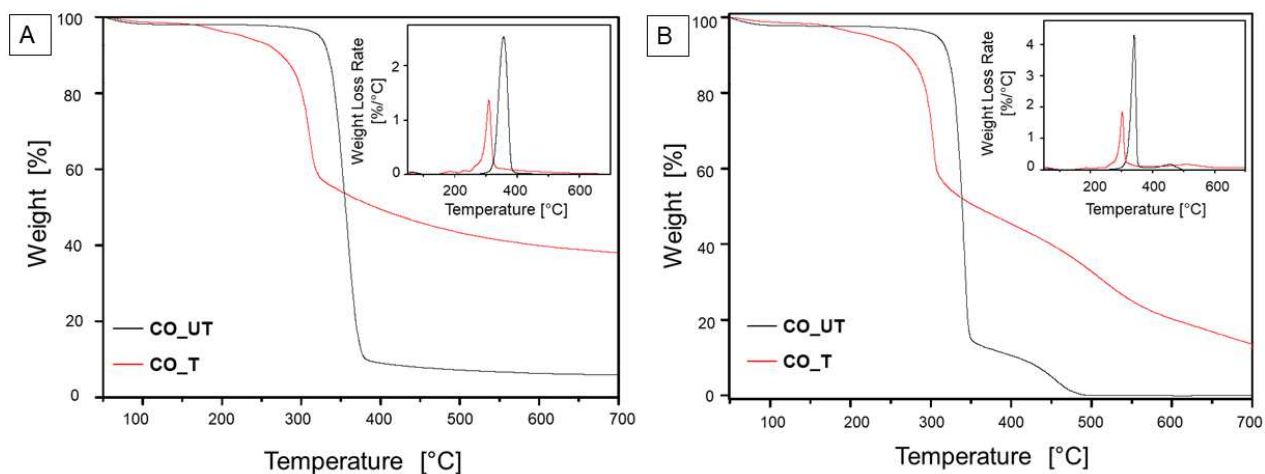
416 Table 4 collects the corresponding data in terms of  $T_{onset}$ ,  $T_{max}$  (corresponding to the peak(s) in dTG

417 curves) and related residues and final residue at 700°C. For both the environments, the weight loss  
418 up to 100°C, due to absorbed moisture in all samples, was not considered for this degradation study.  
419 In nitrogen, the TG curves of untreated cotton sample show the onset degradation temperature at  
420 about 310°C, together with its maximum mass loss rate at about 360°C, due to depolymerization by  
421 trans-glycosylation reactions. The coated fabric shows an anticipation in the onset degradation  
422 temperature, reaching the maximum mass loss rate at 275°C: this finding is attributed to the earlier  
423 degradation of the phosphorus-containing compound that catalyses the decomposition of cotton  
424 towards the formation of a carbonaceous residue (char). This latter increases the thermal stability of  
425 the fabric: in fact, at the end of the test, the char residue achieves 38%, significantly higher than  
426 pure cotton, for which the residue is below 6%.

427 In air, the thermo-oxidation of cotton takes place in a similar way: the only difference is for the  
428 appearance of a second degradation step at high temperatures ( $T_{\max 2}$ : 460°C). This phenomenon can  
429 be attributed to the oxidation of the char formed during the first step and of all the hydrocarbon  
430 species still present [56]. Once again, the hybrid coating is responsible for the decrease of both  
431  $T_{\text{onset}}$  and  $T_{\max 1}$  as well as for the increase of the residues at  $T_{\max 1}$ ,  $T_{\max 2}$  and 700°C: these findings  
432 confirm the protective effect exerted by the formed stable char.

433 Compared to untreated cotton control, the effectiveness of the silica-based coating as a flame  
434 retardant for cotton, directly attributable to the considerably higher energy and ionic character of the  
435 Si-O bond (443.7 kJ/mol) relative to the C-C bond (345.7 kJ/mol) [57], is indicated by a substantial  
436 lowering of the decomposition temperature, due to the earlier degradation of the phosphorus  
437 contained in the modified precursor, which is able to catalyse the dehydration of the treated cotton  
438 to form the intumescent char. As confirmed by TGA results, the higher the residue in the silica-  
439 phosphorylated cotton, the lower is the amount of volatile products obtained upon decomposition of  
440 the samples during the test.

441



442

443 **Fig. 7.** TG and dTG curves of CO\_UT and CO\_T samples, in: **A.** nitrogen and **B.** air atmospheres.

444

445 **Table 4.**

<i>Atmosphere: Nitrogen</i>						
<b>Sample</b>	<b>T<sub>onset</sub> (°C)</b> (s)	<b>T<sub>max1</sub><sup>*</sup></b> (°C)	<b>Residue</b> @T <sub>max1</sub> (%)	<b>T<sub>max2</sub><sup>*</sup></b> (°C)	<b>Residue</b> @T <sub>max2</sub> (%)	<b>Residue</b> @700°C (%)
CO_UT	310	360	40	/	/	5.8
CO_T	275	310	70	/	/	38
<i>Atmosphere: Air</i>						
CO_UT	300	340	46	460	3.2	/
CO_T	260	300	73	520	30	12

446 TG data for CO\_UT and CO\_T in nitrogen and air.

447 \* from dTG curves

448

### 449 3.6 Cone calorimetry tests

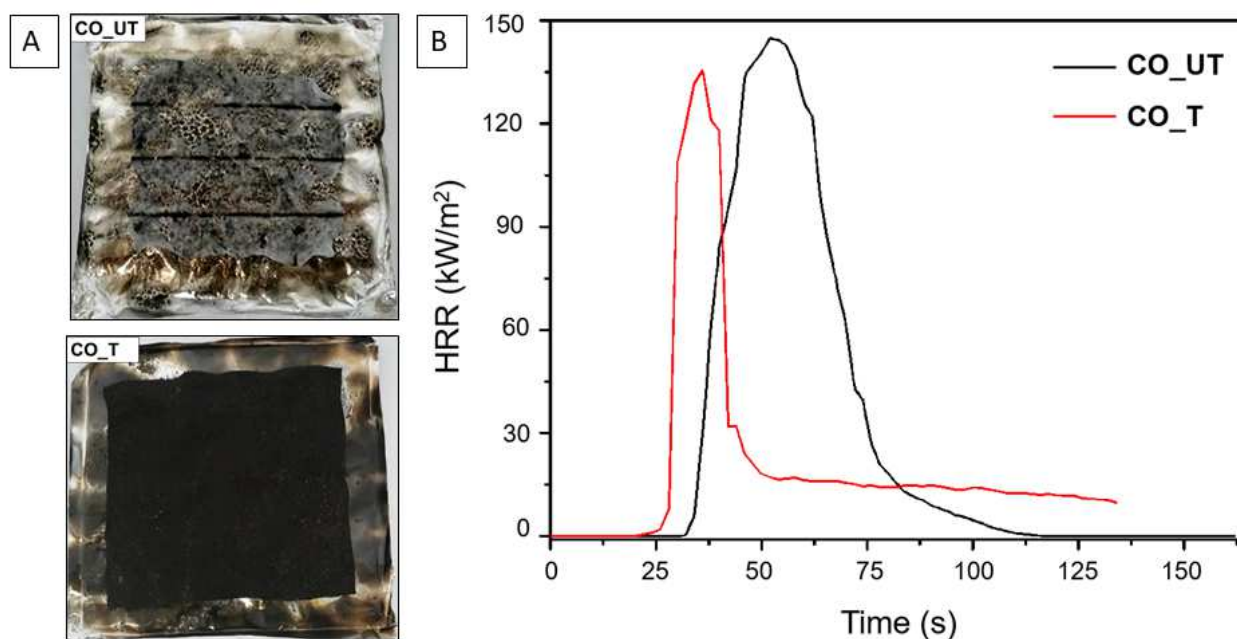
450

451 The forced-combustion behaviour of cotton samples was investigated through cone calorimetry  
452 tests, measuring the time to ignition (TTI), the peak heat release rate (pkHRR), the total heat release  
453 (THR) and the final residue (%), as well as CO and CO<sub>2</sub> yields (%).

454 The curves of HRR vs. time for control and silica-coated fabric are shown in Fig. 8B. From Tab. 5,  
455 it can be seen that if compared to untreated cotton, the coated fabric shows a reduction in both heat  
456 release rate peak (pkHRR) and in the total heat release (THR). In fact, with respect to the uncoated  
457 sample, in the treated fabric pkHRR decreases from 154 to 135 kW/m<sup>2</sup>, corresponding to an  
458 approximately 12% reduction. The THR also drops significantly, going from 3.9 down to 2.3  
459 MJ/m<sup>2</sup>. In the case of coated sample, it is worthy to note that after ignition, the HRR value increases  
460 rapidly in a very short time (from 25 to 40 s) and then decreases sharply. This behaviour is  
461 attributable to the formation of an intumescent char instantly after ignition by the phosphorus-  
462 containing silica coating, indicating that more cotton fabric participates in the carbonization  
463 process, due to the presence of the deposited coating. Consequently, less degradation products that  
464 serve as “fuel” go into the gas phase, hence lowering the pkHRR and THR values. In addition, in  
465 order to evaluate the fire performance index (FPI), the ratio between final residue and pkHRR  
466 values for treated and untreated samples was calculated. The FPI value of the control cotton is  
467 0.023 %/s, whereas that for silica coated cotton is 0.76 %/s. The higher FPI value for the coated  
468 cotton sample justifies the higher amount of final residue and the shorter time to ignition with  
469 respect to the untreated counterpart. Based upon the aforementioned fire behaviour, it is believed  
470 that the formation of intumescent char layer is responsible for suppressing fire propagation at the  
471 selected heat flux, or greatly inhibiting the amount of flammable gases available for combustion.  
472 Finally, through CO and CO<sub>2</sub> analysis it is possible to provide useful information on the mechanism  
473 of decomposition of cotton fabrics, since low CO<sub>2</sub>/CO ratio means low conversion of CO to CO<sub>2</sub>,  
474 thus suggesting inefficiency of combustion. When cotton fabrics were treated with PGPTES, the

475 CO production changed a little, whereas the CO<sub>2</sub> production was decreased, leading to a remarkable  
476 decrease of CO<sub>2</sub>/CO ratio (19.5). This suggests that the designed flame retardant mainly acts in  
477 condensed phase. It should be remarked that the char residues from cone calorimeter tests, reported  
478 in Figure 8A, are consistent with high-temperature residues obtained by TG analysis. The poor  
479 residue from the neat sample was completely broken, hence confirming the low charring ability of  
480 cellulose. On the other hand, the residue of the coated sample shows a coherent and dense char,  
481 maintaining a compact structure and its original texture. This is a direct consequence of the silica  
482 precursor formulation containing phosphorus and nitrogen. In fact, both species can synergistically  
483 act [28,51], catalysing the formation of the char layer that limits the heat and mass transfer, thus  
484 reducing the formation of flammable gases. At the same time, this char was made more stable by  
485 the beneficial presence of silica that does not allow the fire spread.

486



487

488

489 **Fig. 8. A.** Residues of CO\_UT and CO\_T from cone calorimetry tests performed at 35 kW/m<sup>2</sup>; **B.**  
490 Heat release (HRR) curves of CO\_UT and CO\_T.

491

492

493

494 **Table 5.**495 Combustion data of CO\_UT and CO\_T from cone calorimetry tests performed at 35 kW/m<sup>2</sup>

Sample	TTI (s)	Flame out (s)	pkHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	Residue (%)	CO (%)	CO <sub>2</sub> (%)	CO <sub>2</sub> /CO
CO_UT	43±2	75	154±4	3.9±0.1	1	0.0014	0.20	143
CO_T	34±2	48	135±3	2.3±0.1	26	0.0087	0.17	20

496

497

498 **3.7 Flammability tests**

499

500 In order to evaluate flame retardant performance, the uncoated and coated fabrics were subjected to  
501 horizontal and vertical flame spread tests. The images of the burned samples, together with the  
502 flammability data (after flame time, afterglow time and residue (%)), for both vertical and  
503 horizontal configurations, are presented in Table 6. At the end of the tests, the residues the uncoated  
504 fabrics have been completely destroyed, leaving only few amounts of ash, whereas for the treated  
505 sample there was only smoulder progression of fire that stopped before the scribed line for  
506 measurement. More in detail, in horizontal configuration, immediately after ignition, on the  
507 untreated sample a vigorous flame appears for about 23 s, followed by 139 s of afterglow that did  
508 not leave any residue. Conversely, the treated fabric sample shows no visible after-flame time, and  
509 very short after-glow time (8 s) and achieves self-extinction a few seconds after the flame  
510 application. As a result, at the end of combustion, the residue is 99.5% and the Flammability  
511 Performance Index (FPI) is 12.44%/s. Also in vertical configuration, the untreated cotton fabric is  
512 fully consumed during the test; conversely, the treated sample completely stops the flame  
513 propagation almost as soon as the flame is removed, showing neither afterflame, nor afterglow and

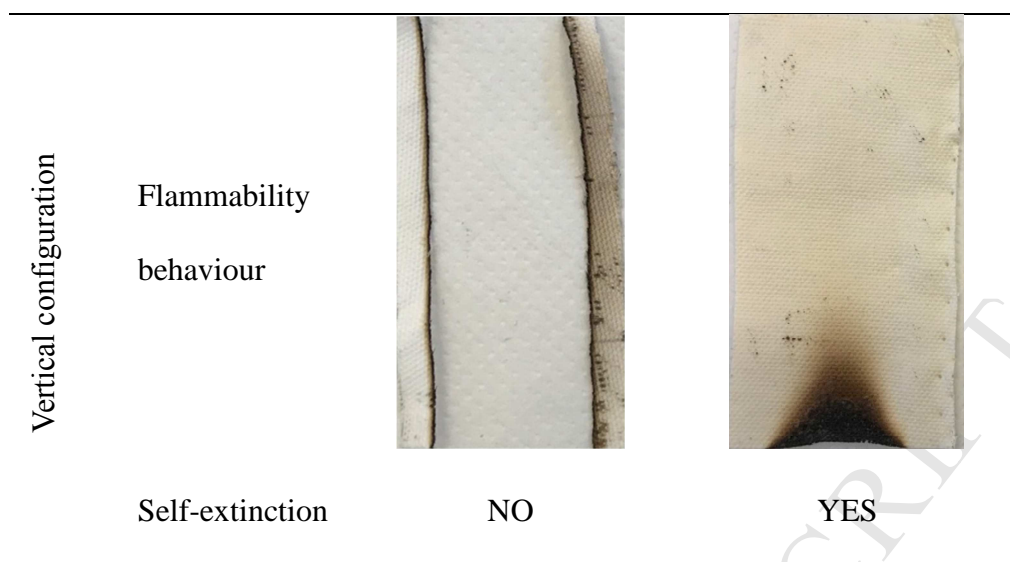
514 obtaining self-extinguishing classification. Once again, the results confirm the good behaviour of  
 515 the phosphorous and nitrogen containing sol-gel coating onto cotton fibres, as a dehydrating and  
 516 char-forming layer, which hinders heat, fuel and oxygen transmission by creating a ceramic barrier  
 517 onto the treated fabric surface from further burning.

518

519 **Table 6**

520 Flammability behaviour and data related to the horizontal and vertical tests of CO\_UT and CO\_T  
 521 samples.

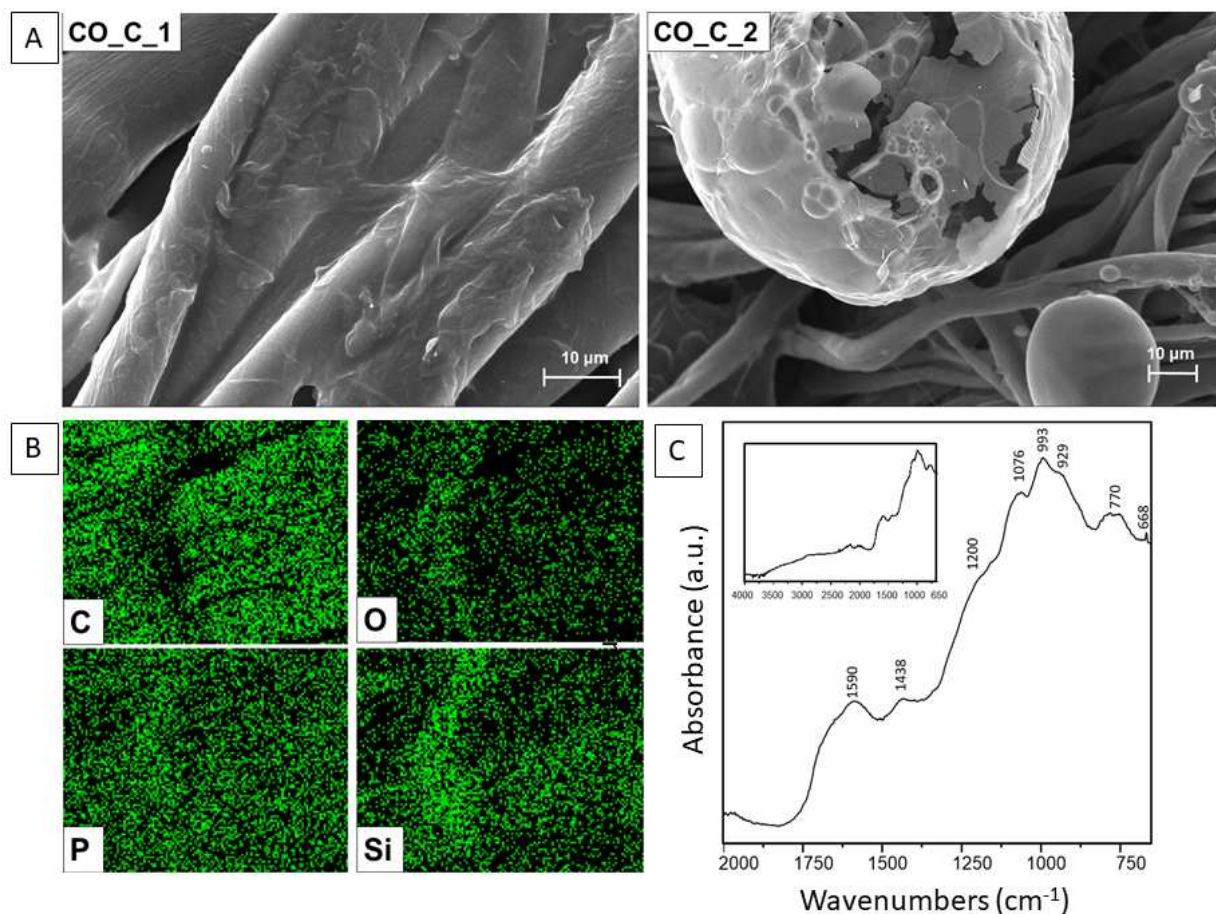
<b>Data</b>		<b>CO_UT</b>	<b>CO_T</b>
Horizontal configuration	t <sub>1</sub> (s)	<b>23</b>	<b>8</b>
	t <sub>2</sub> (s)	<b>76</b>	<b>0</b>
	Total burning time (s)	<b>139</b>	<b>8</b>
	Residue (%)	<b>0</b>	<b>99.5</b>
	FPI (%/s)	<b>0</b>	<b>12.44</b>
	Self-extinction	<b>NO</b>	<b>YES</b>



522

523 In order to understand the char composition and to investigate the mechanism of flame retardancy,  
 524 achieved with the hybrid coating, after the vertical flame spread tests, SEM analysis and ATR-FTIR  
 525 spectra of burned coated cotton fabrics were carried out. SEM micrographs (Figure 9) show that the  
 526 charred region in the treated sample still maintains the shape of the original fibres and its weave  
 527 structure, displaying only minor shrinkage. Fibres look very rough and show many bubbles on their  
 528 surface: these findings are attributed to swelling and expansion of the coating due to its intumescent  
 529 effect. It's possible to observe big bubbles on the surfaces of charred layer of FR cotton sample.  
 530 These bubble char not only inhibits the release of flammable gases from cellulose degradation but  
 531 also prevents the heat source to convey heat to the cellulosic substrate ~~and insulates the oxygen~~  
 532 ~~source~~ [52]. The intumescent layer protects the fibres from further burning, preserving the woven  
 533 structure and fibre integrity, which is responsible for the self-extinguishing phenomenon of cotton.  
 534 Besides, the results of the elemental analysis carried out on the same residue still indicate the  
 535 presence of phosphorous and silicon, homogeneously distributed, notwithstanding the presence of  
 536 carbon and oxygen, as for the control sample. This good performance was mainly produced by three  
 537 components of developed molecule: first, the phosphorous group able to release P-based acids that  
 538 catalyse the dehydration of cotton to form char. This char is able to prevent heat, fuel, and oxygen  
 539 from being transferred from the flame to the fabric. Second, the deoxyribose units acted both as a

540 carbon source and blowing agents, with which a (poly)saccharide dehydrates to form char and  
 541 releases water upon heating. Third, the nitrogen-containing base released ammonia, which can  
 542 further induce char development and produce non-combustible gases such as  $N_2$  and  $CO_2$ .



543  
 544 **Fig. 9.** A. SEM images of the residues of CO\_T at different magnifications, coded as \_1, \_2, for  
 545 x2.50 K, x1.00 K, respectively, B. EDX images of the treated sample; C. ATR-FT IR of treated  
 546 cotton fabric pyrolyzed at 600°.

547  
 548 To investigate the chemical composition of the burned sol-gel coated fabric after the vertical flame  
 549 spread test, the sample was examined by ATR-FTIR: its spectrum is shown in Figure 9C and  
 550 detailed band assignments are provided alongside the spectrum. The presence of aromatic-type  
 551 structure was confirmed by the intense band at around 1590 cm<sup>-1</sup> and a shoulder at 1200 cm<sup>-1</sup>,  
 552 ascribed to the presence of polynuclear aromatic structures (-C=C- stretching) [53] and the vibration

553 of CH groups, out of plane bending, respectively. The shoulder peak at  $1200\text{ cm}^{-1}$  may also  
554 comprise the signal assigned to the functionality of a phosphorus-nitrogen structure. Furthermore,  
555 the peaks in the region  $1000\text{--}650\text{ cm}^{-1}$  may be assigned to the out of plane deformation vibrations  
556 of the ring [61]. Finally, the peaks at  $1070\text{ cm}^{-1}$  are ascribable to the Si–O–Si stretching vibration  
557 that confirms the formation of a silica matrix in the char. These characteristic absorptions are in  
558 accordance with depolymerization of cellulose and formation of char [62]. From both analyses it is  
559 clear that the char of the treated sample seems to consist of phosphorous, carbon and silicon-rich  
560 compounds. The carbonaceous char that originates on the surface of the burning fabric during  
561 combustion is thus covered by silicates and phosphonates, hence creating an excellent physical  
562 barrier, which protects the substrate from heat and oxygen, and slowing down the escape of  
563 flammable volatiles generated during cellulose degradation.

564

#### 565 **4. Conclusions**

566

567 A novel sol-gel based flame retardant containing phosphorus, nitrogen, and silicon was synthesized  
568 successfully, and its chemical structure was fully characterized by Fourier transform infrared  
569 spectrometry and nuclear magnetic resonance spectrometry ( $^1\text{H}$  NMR and  $^{13}\text{C}/^{31}\text{P}$  NMR). After its  
570 application on cotton fabric, the combustion behaviour of the treated sample was investigated,  
571 confirming that the so obtained coating acts as an efficient flame retardant in the condensed phase.  
572 In particular, the presence of PGPTES lowers the decomposition temperature and favours the  
573 formation of char after pyrolysis; in addition, in forced combustion tests, the coating is responsible  
574 for the increase of TTI and the reduction of both HRR value and CO/CO<sub>2</sub> ratio for treated cotton  
575 sample. These results demonstrated the formation of a compact and thermostable char residue that  
576 effectively improved the thermal stability of cotton fabrics by hindering the formation of volatile  
577 species and favouring the creation of a stable char. It can be concluded that the hybrid GPTES-  
578 modified precursor can be potentially used as a new flame retardant replacing halogen-based

579 finishes in the field of flame retardant textile materials. Combining the above-mentioned  
580 advantages, it emerges as a promising candidate for the design of a next-generation of hybrid  
581 materials with breakthrough flame retardant performances. Further research will be developed in  
582 order to investigate the washing fastness of the proposed sol-gel coating and its influence on the  
583 mechanical properties of treated cotton fabrics.

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ACCEPTED MANUSCRIPT

**HIGHLIGHTS**

- NMR analysis confirms the functionalization of GPTES sol-gel precursor with PMIDA.
- PMIDA acts as nitrogen and phosphorous source in the P/N flame retardant synergism.
- The concurrent presence of Si, P and N enhances cellulose dehydration mechanism.
- The final residue for treated cotton sample, after cone calorimetry test, is 26%.
- Self-extinguishing properties are achieved by the treated cellulose-based fabric.