

1 **Thermal and flame retardant behaviour of cotton fabrics treated with a novel nitrogen-**
2 **containing carboxyl-functionalized organophosphorus system**

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10

11 **Abstract**

12 In this paper, a nitrogen-containing carboxyl-functionalized organophosphorus oligomer was
13 immobilized onto cotton fabrics using 1,2,3,4-butanetetracarboxylic acid as an environmentally-
14 friendly binder, in the presence of sodium hypophosphite, used as a catalyst, and triethanolamine, as
15 a reactive additive for adjusting the pH of the mixture and contributing to phosphorous-nitrogen
16 synergism. In addition, with the aim of reducing the formation of insoluble calcium salt during
17 home laundering, due to the free carboxylic acid groups bound to the cotton fabric, the treated
18 samples were recoated employing three sol-gel precursors, namely 3-aminopropyltriethoxysilane,
19 tetraethoxyorthosilane and 3-glycidyloxypropyltriethoxysilane. Untreated and treated samples were
20 thoroughly characterized to understand the chemical structure of the coatings, the bonding with the
21 cellulosic substrate and the related surface morphology. The thermal behaviour was investigated by
22 thermogravimetric analysis, horizontal and vertical flame tests and forced combustion tests. The
23 results showed very good performances of the treated fabrics that were able to achieve self-
24 extinction.

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Keywords: N-(Phosphonomethyl)iminodiacetic acid; sol-gel; self-extinguishing; textile finishing;
cotton fabric

1. Introduction

Although it has been an important tool throughout human history, fire can generate dramatic consequences if not properly controlled. According to the data from 2016 National Fire Protection Association (NFPA) (Haynes, 2017), the public fire departments in the U.S. responded to 1,342,000 fires that caused 3,390 civilian deaths, 14,650 civilian injuries, and an estimated \$10.6 billion loss in direct property. Since a wide range of commonly used materials is flammable, this means that the use of flame retardants can reduce these hazards and significantly contribute to save lives and resources. As the main component of cotton, cellulose is employed for manufacturing apparel, home furnishings and industrial products, even though its low limiting oxygen index (18%) and combustion temperature (360-425°C) make this material highly flammable (Wakelyn et al., 2006). To overcome this drawback, a chemical modification of the cellulose structure is necessary.

In the last years, several treatments have been extensively studied to modify the combustion characteristics of cotton, in order to meet fire safety regulations and expand the use of cotton in textile applications that require flame retardancy. The majority of these flame retardant treatments can be classified into four distinct groups, as they can be based on the use of halogenated organic, inorganic, organophosphorus, and nitrogen formulations (T.-M. Nguyen, Chang, Condon, & Smith, 2014). Despite their effectiveness, some of these products, like halogen-containing compounds, turned out to be hazardous for human health, due to the use of textile materials that are typically in close contact with skin. The aforementioned disadvantages stimulated the scientific community towards the development of phosphorus-based compounds, which seem less toxic and may represent a suitable alternative to halogen-based formulations (Salmeia & Gaan, 2015; Grümping, Opel, & Petersen, 2007). In the last decades, phosphorus has become the subject of several research

studies for cotton treatments (H. Yang & Yang, 2005), as P-containing flame retardants are able to convert into phosphorus-based acids. This promotes the formation of non-volatile polyphosphoric acids that can react with the decomposing polymer, by both dehydration and esterification, enhancing the char formation (A. Richard Horrocks, 1996). The latter acts as a barrier and protects the treated polymer from the attack of radiant heat and oxygen, favouring the combustion extinction. Several studies have shown that the phosphorus-nitrogen combination increases flame resistance in cotton textiles, using a lower phosphorus content than that required when P is employed alone (T.-M. D. Nguyen, Chang, Condon, Uchimiya, & Fortier, 2012) and releasing low amounts of toxic gases. One of the action mechanisms proposed for P-N containing flame retardants involves the Lewis acidity of electrophilic phosphorus, which promotes cellulose dehydration and char formation (A R Horrocks, 2008b; A R Horrocks, 2008a). Due to the nucleophilic attack on the phosphate, nitrogen favours the formation of polymeric species containing P-N bonds, characterized by a more polar character than P-O bonds. The enhanced electrophilicity of the phosphorus atom increases its ability to phosphorylate C(6) primary hydroxyl groups of cellulose chains. The actions of organophosphorus retardants are ascribable to: a) nitrogen-synergized phosphorylation of cellulose in the C(6) position to block levoglucosan formation, b) Lewis acid-catalysed dehydration to char, which is not advantageous to levoglucosan formation and c) cellulose cross-linking in order to promote char formation. The hydroxyl groups of the cellulose fibres can react with N-methylol reactive groups included in the structures of organophosphorus compounds in a condensation reaction, resulting in the formation of covalent bonds able to strongly increase the adhesion between finishes and the fibre surface. Among the various phosphorus-based flame retardant agents developed, tetrakis(hydroxymethyl) phosphonium chloride (THPC) and N-methylol dimethylphosphono propionamide (MDPA) have been the most useful halogen-free flame retardants (FRs), employed as cotton fabric flame-retardant finishes. However, these types of FRs have the disadvantage of formaldehyde release, that is considered a carcinogen compound by IARC, responsible for nasopharynx cancer and leukemia (World Health Organization, 2012). Thus,

78 its mutagenic activity makes it imperative to find alternative formaldehyde-free finishes. As binders
79 for organophosphorus FRs, either resins or reactants with at least two carboxylic groups have been
80 studied. Yang et al. investigated the potentiality of 1,3-dimethylol- 4,5-dihydroxyethylene urea
81 (DMDHEU) as a binder in flame retardant finishing (W. Wu & Yang, 2003; C. Q. Yang & Wu,
82 2003a), while experiments with 1,2,3,4-butanetetracarboxylic acid (BTCA) applied to cotton or
83 cotton blends were carried out (C. Q. Yang & Wu, 2003b; X. Wu, Yang, & He, 2010).
84 Unfortunately, as for the aforementioned FRs, DMDHEU tends to release formaldehyde and,
85 consequently, it does not meet sustainable chemistry requirements. Conversely, BTCA, a well-
86 known non-formaldehyde crosslinking reagent containing four carboxylic acid groups, thermally
87 treated in presence of a phosphorus-based catalyst, is able to form effective crosslinks in cotton
88 fabrics, through an esterification mechanism that follows a two steps reaction: first, cyclic
89 anhydrides are formed and hence, during the second step, they react with the hydroxyl groups (-
90 OH) of the cellulosic substrate, giving rise to ester bonds (Huang, Song, Xing, & Dai, 2010). The
91 role of sodium hypophosphite (SHP) is to catalyse the formation of linkages between
92 polycarboxylic acid and cellulose, while cellulose phosphorylation is one of the parallel reactions.
93 Recently, flame retardant properties were achieved by immobilizing phosphorus-based oligomers
94 (Brancatelli, Colleoni, Massafra, & Rosace, 2011) or nanoparticles (Guido et al., 2013) onto the
95 textile surface; in this context, the sol-gel technique has been reported as a promising tool for the
96 preparation of hybrid organic-inorganic nanocomposite coatings (Malucelli, 2016).

97 The aim of this study is to investigate the flame retardant action of N-(phosphonomethyl)
98 iminodiacetic acid (PMIDA), a molecule bearing two carboxylic groups and one amine group, as a
99 nitrogen-containing carboxyphosphonate, suitable for improving the flame retardancy of cellulose-
100 based materials. In order to avoid the disadvantage of treating cotton fibres in an excessively strong
101 acidic medium originated by the PMIDA aqueous solutions, triethanolamine (TEA), a tertiary
102 amine containing three polar hydroxyl groups joined by a two-carbon alkyl chain, was used. In
103 addition, this compound may contribute to the phosphorus-nitrogen (P-N) synergistic action in the

104 flame retardancy of cotton fabric. To promote the immobilization of finishes onto cellulose
105 macromolecules, BTCA was used in combination with SHP, that acts as the reaction catalyst. When
106 the fabric treated with this polycarboxylic acid is laundered in tap water, the free carboxyl groups
107 on the cotton surface can form insoluble calcium salts, turning out in a leaching of the coating [14]
108 (C. Q. Yang & Wu, 2003b). To avoid this problem, in a second step, the treated cotton sample was
109 recoated employing two different hybrid sol-gel solutions, namely 3-aminopropyltriethoxysilane
110 (APTES), or a mixture of tetraethoxyorthosilane (TEOS) and 3-glycidyloxypropyltriethoxysilane
111 (GPTES) precursors. In particular, GPTES and APTES were selected because their epoxy and
112 amine functional groups are known to react with carboxylic acids, resulting in the formation of
113 ether or amide bonds, respectively. These second layers act as a barrier that could increase the
114 washing fastness of the treatments. Both hybrid sols, in fact, promote crosslinking during the
115 formation of sol-gel networks exhibiting high flexibility, excellent mechanical properties, no
116 cytotoxic activity (Plutino et al., 2017), and good flame retardant performances (Alongi, Colleoni,
117 Rosace, & Malucelli, 2012). To investigate the morphology and the surface composition of fabrics
118 after the proposed treatments and to verify the presence of the deposited layers onto cotton fabrics,
119 Scanning Electron Microscopy (SEM) and FT-IR spectroscopy were carried out. Weight percentage
120 changes between treated and untreated samples and between washed and unwashed samples were
121 determined for evaluating the coating durability. The thermal and thermo-oxidative behaviour of the
122 treated samples were assessed by Thermogravimetric analysis (TGA) in nitrogen and in air,
123 respectively. Furthermore, the flame retardancy conferred to the cotton fabrics due to the character
124 of the deposited coatings was tested using both horizontal and vertical flammability tests. These
125 measurements were also repeated after one standardized washing cycle, in order to check the
126 stability and the durability of the finishing. The effectiveness of this novel formaldehyde-free and
127 halogen-free flame-retardant is thoroughly discussed on the basis of the obtained experimental
128 results.

129

130 2. Experimental part

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132 2.1. Materials

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134 Desized, scoured and bleached plain weave cotton fabric (100%, 331 g/m²) was kindly supplied
135 by Mascioni SpA (Cuvio, Varese, Italy). 1,2,3,4 butanetetracarboxylic acid (BTCA), sodium
136 hypophosphite (SHP), N-(Phosphonomethyl)iminodiacetic acid hydrate (PMIDA, 97%, MW
137 227.11), hydrochloric acid (36.5–38.0%), ethanol ($\geq 99.8\%$), and all the sol-gel precursors, namely
138 3-aminopropyltriethoxysilane (APTES, $\geq 98\%$), tetraethoxysilane (TEOS, $\geq 98\%$) and 3-
139 glycidoxypropyltriethoxysilane (GPTES, $\geq 98\%$), were supplied by Sigma Aldrich (Germany). All
140 chemicals were of analytical reagent grade and were used without further purification. The cotton
141 samples were washed in 2% non-ionic detergent at 40°C for 20 min, then rinsed several times with
142 deionized water, dried and kept into a drier for storage. The cleaned samples were conditioned
143 under standard atmospheric pressure at $65 \pm 4\%$ R.H. and $20 \pm 2^\circ\text{C}$ for at least 24 h prior to all the
144 tests.

145

146 2.2. FR preparation

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148 30 g (0.1321 mol) of PMIDA were mixed with 10 g (0.043 mol) of BTCA in the presence of
149 11.5 g (0.11 mol) of sodium hypophosphite (SHP), used as a catalyst. The solution pH was adjusted
150 to 3, under vigorous stirring, with TEA (Triethanolamine) and then heated to 50°C (to promote the
151 solubilisation of the used chemicals). The sol solutions, employed as second layers of treated FR
152 cotton fabrics, were synthesized according to the following procedure:

153 (a) APTES sol: 2.4 ml of APTES (0.01 mol) were hydrolysed in the presence of 2 ml (0.0002 mol)
154 of HCl (0.1 M) in 95.6 ml of deionized water, obtaining a 0.1 M solution.

155 (b) GPTES/TEOS (25:75) sol was obtained adding dropwise 0.70 ml of GPTES (0.0025 mol) and

156 1.68 ml of TEOS (0.0075 mol) in 60 mL of water, in the presence of 4 mL of HCl (0.1 M) suitable
157 for promoting hydrolysis (pH 3). After vigorous mechanical stirring for 4 h at room temperature,
158 the mixture became transparent and homogeneous. Finally, distilled water was added to reach a
159 total volume of 100 ml.

160

161 2.3. Cotton fabrics treatments

162

163 A two-stage procedure was designed for treating the textile samples. First, cotton samples (20 ×
164 30 cm) were impregnated with the finishing solutions and afterwards passed through a two-roll
165 laboratory padder (Werner Mathis, Zurich, Switzerland) working with 3 bar nip pressure in order to
166 achieve 70% wet pick-up. After drying at 80°C for 10 min, textile samples were cured at 170°C for
167 2 minutes. This layer was used as flame retardant coating for the cotton fabrics coded as CO_A.
168 Successively, some of these so-treated samples were re-coated with sol solutions, in order to react
169 with the free carbonyl groups onto cellulose surface; thus, FR pre-treated cotton samples were
170 immersed into the APTES sol or into the TEOS/GPTES sol, obtaining the samples coded as CO_B
171 and CO_C, respectively. Finally, the cotton fabrics were dried and cured following the same
172 conditions used for the first layer.

173 All cotton samples were weighed before (W_0) and after the treatment (W_1), using a Mettler
174 balance ($\pm 10^{-4}$ g), and the values were fitted to the Equation 1 to obtain add-on levels.

$$175 \quad A = \frac{W_1 - W_0}{W_0} \times 100 \quad \text{Eq. 1}$$

176 For each sample, an average value was determined on the basis of the three measured data, with
177 the standard deviation always below 2%. The obtained add-on values are summarized in Table 1.

178

179

180

181 **Table 1.**

182 Molar ratio and molar concentration of solutions used for the treated cotton samples.

Code	1 st layer		2 nd layer		Add on (wt% owf)	Weight loss after 1 washing cycle (wt% owf)
	Chemicals	Molar ratio	Chemicals	Molar concentration (M)		
CO_A	PMIDA, BTCA, SHP, TEA	3:1:2.5:1.6	/	/	23.4	/
CO_B	PMIDA, BTCA, SHP, TEA	3:1:2.5:1.6	APTES	0.1	28.2	8.4
CO_C	PMIDA, BTCA, SHP, TEA	3:1:2.5:1.6	TEOS/GPTES	0.1	24.9	8.7

183

184 2.4. Characterization techniques

185

186 The carbonyl band absorbance in the infrared spectra was normalized against the 1317 cm⁻¹
187 band associated with a C–H bending mode of cellulose. To investigate the chemical structure of
188 cotton fabrics, Fourier transform infrared spectroscopy (FTIR) spectra of untreated and treated
189 cotton fabric were collected and examined. The spectra were recorded at room temperature in the
190 range from 4000 to 650 cm⁻¹ with 64 scans and a resolution of 4 cm⁻¹ using a Thermo Avatar 370
191 spectrophotometer, equipped with attenuated total reflection (ATR) accessory and a ZnSe crystal.
192 The collected spectra were normalized against the 1314 cm⁻¹ band, associated with the C-H bending
193 mode of cellulose. The surface morphology of the treated samples was studied using a LEO-
194 1450VP Scanning Electron Microscope (beam voltage: 5 kV), equipped with an X-ray probe
195 (INCA Energy Oxford, Cu-Ka X- ray source, k= 1.540562 Å), which was utilized for performing
196 elemental analysis. Fabric pieces (0.5 cm x 0.5 cm) were cut and fixed to conductive adhesive tapes
197 and gold-metallized. Also the residues of treated fabric, after combustion, were subjected to SEM-

EDX investigation. The thermal and thermo-oxidative stability of the fabrics was evaluated by thermogravimetric (TG) analyses from 50 to 700 °C with a heating rate of 10°C/min, in nitrogen and in air (gas flow: 60 mL/min for both the atmospheres). To this aim, a TAQ500 thermogravimetric balance was used, placing the samples in open alumina pans (ca. 10 mg). The experimental error was $\pm 0.5\%$ on the weight and $\pm 1^\circ\text{C}$ on the temperature.

The flame retardancy properties of the prepared samples were measured using flame spread tests performed both in horizontal and vertical configurations. In the first case, the flame was applied on the short side of the specimen (50 mm); two horizontal lines were drawn on the specimens (at 25 and 75 mm from the side on which the flame was applied, respectively) and the time (t_1 and t_2) necessary to the flame to reach them was measured. Besides, other relevant parameters, such as total burning time and final residue, were evaluated.

Alternatively, when the test was performed in vertical configuration, a methane flame was applied for 5 s at the bottom of a fabric specimen (50 mm x 100 mm), repeating the test 3 times for each formulation in order to get reproducible data. A Flammability Performance Index (FPI, %/s) was also calculated as the ratio of final residue to the total burning time and used as an evaluation parameter: the higher the FPI values, the better is the flame retardancy performance (Alongi, Ciobanu, & Malucelli, 2011). Cone calorimetry (Fire Testing Technology, FTT) was used to investigate the forced-combustion behaviour of square fabric samples (50 mm x 50 mm x 0.5 mm). The measurements were carried out under a 35 kW/m² irradiative heat flow in horizontal configuration, following the procedure described elsewhere (Tata, Alongi, & Frache, 2012). The experiments were repeated four times for each material investigated to ensure reproducible and significant data; the experimental error was within 3%. Prior to flammability and forced-combustion tests, all the specimens were conditioned at $23 \pm 1^\circ\text{C}$ for 48 h at 50% R.H. in a climatic chamber. The following parameters were registered: time to ignition (TTI, s), flame-out time (FO, s), peak of heat release rate (PHRR), heat release rate (HRR, kW/m²), total heat release (THR, assessed at the end of the test, MJ/m²), ratio of carbon dioxide and carbon monoxide yields, and

224 final residue (%). The durability of the modified cotton fabrics was evaluated by modified standard
225 conditions (EN ISO 6330:2000) using tap water, containing approximately 10 ppm calcium, at
226 40°C for 30 minutes. The weight loss of the bilayer coated samples after one washing cycle (WLW,
227 wt. %), was measured using a Mettler balance (10^{-4} g), according to the following Equation 2:

$$228 \quad WLW = \frac{W_{TW} - W_T}{W_T} \times 100 \quad \text{Eq. 2}$$

229 where W_T and W_{TW} are the dry weights of the treated cotton samples before and after the washing
230 cycle, respectively. All the fabrics were weighted five times with the standard deviation always
231 below 2%. The calculated weight losses after 1 washing cycle are collected in Table 1.

232

233 **3. Results and discussions**

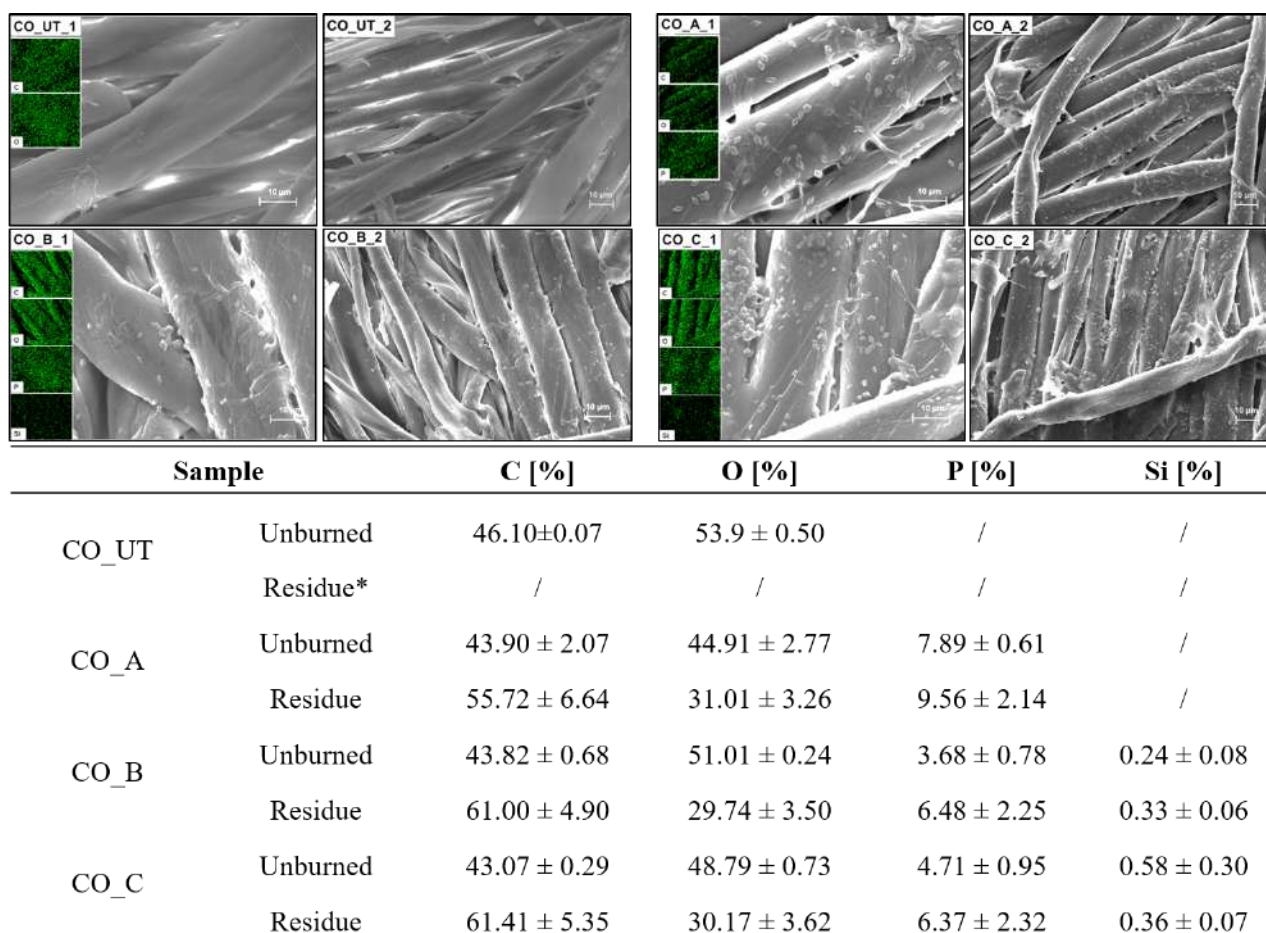
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235 *3.1. SEM–EDX analysis*

236

237 The topical morphology, composition and homogeneous distribution of flame retardant coatings
238 on the cotton fabric were inferred from the Scanning Electron Microscopy (SEM) and the Energy
239 Dispersive X-ray (EDX) analysis results. Two magnifications of treated and untreated cotton fabrics
240 are shown in Figure 1. The untreated cotton sample exhibits a normal spiral structure with the
241 presence of natural folds, running parallel along the fibre axis, as well as a smooth surface. During
242 the curing treatments, the SHP-catalysed 1,2,3,4-butanetetracarboxylic acid forms covalent bonds
243 with the hydroxyl groups of cotton surfaces, increasing the extent of the interaction between
244 adjacent cellulose chains. Furthermore, under the given finishing conditions, the cross-linked
245 cellulose structure enables the fixation of PMIDA on its active groups. As a result, inter-chain
246 connections and aggregates appear clearly visible in the SEM images of the treated fabrics that
247 anyhow preserve the applanate and curled striations of pristine cotton. Through the semi-
248 quantitative EDX investigation (Fig. 1), by employing a high beam voltage (i.e. 20 kV), the

249 elemental composition of treated and untreated samples was investigated. As the technique cannot
 250 detect hydrogen atom, the reference cotton shows exclusively the presence of carbon and oxygen.
 251 Notwithstanding these elements, the treated samples reveal the presence of only phosphorus and
 252 silicon (the latter was observed when silica precursors were used). In addition, as shown by the
 253 elemental maps (inset in Figure 1), elemental analysis confirms a uniform and homogeneous
 254 distribution of the above-mentioned elements on the treated fabric samples.



* No residue was collected after flammability tests

255

256 **Fig. 1.** SEM images and elemental maps of CO_UT, CO_A, CO_B, CO_C at different
 257 magnifications (coded as _1 and _2, for x2.50 K and x1.00 K, respectively) and results (wt.%) of
 258 EDX analysis of untreated and treated samples.

259

260 3.2. FT-IR ATR spectroscopy

261

262 The ATR FT-IR spectra of the treated samples shown in Figure 2 provide supporting evidence
 263 for the structural differences existing between treated fabrics and the untreated one. The frequencies
 264 of major absorption bands are listed in Table 2. CO_UT shows the characteristic spectrum of
 265 cellulose with the hydrogen-bonded OH stretching at ca. 3550–3100 cm⁻¹.

266

267 **Table 2.**

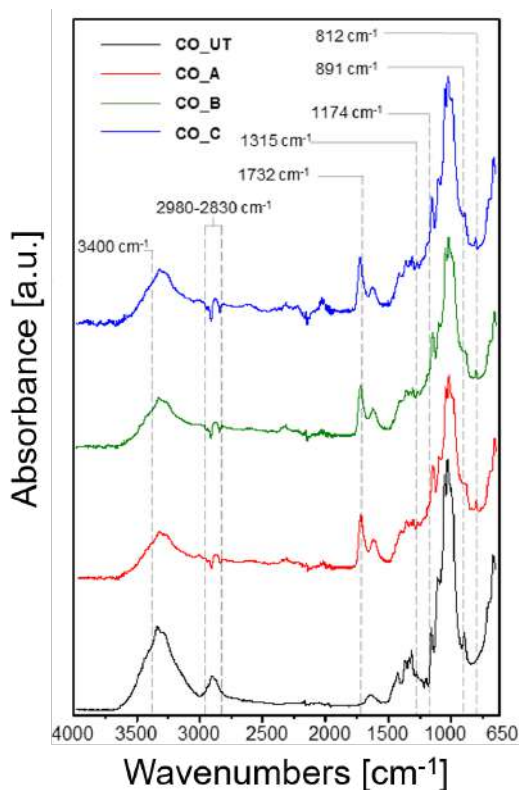
268 Assignments of FTIR peaks of treated and untreated cotton samples.

Band (cm ⁻¹)	Absorbtion	From literature (cm ⁻¹)
3550–3100	ν O-H	3500-3000 (Colleoni et al., 2013)
2980-2830	ν C-H	3000-2800 (Alongi, Colleoni, Malucelli, & Rosace, 2012)
1732	ν_{asym} C=O	1728 (Christian Schramm & Rinderer, 2015)
1315	γ C-H	1315 (Colleoni et al., 2013)
1174	ν P=O	1174 (C. Q. Yang, 2001)
1159	ν_{asym} C-O-C	1159 (Galkina, Ivanov, Agafonov, Seisenbaeva, & Kessler, 2015)
891	ν P-O-C	881 (Nam et al., 2012)
812	γ_w H-P-H	812 (Xiaohong G & Yang, 2000)

269

270 In particular, the OH infrared absorption bands beyond 3400 cm⁻¹ are ascribed to intramolecular
 271 hydrogen bonds, whereas those reported to intermolecular hydrogen bonds are visible at
 272 wavenumbers below 3400 cm⁻¹ (Christian Schramm & Rinderer, 2015). Besides, the stretching
 273 vibrations of CH- and CH₂- bonds of methylene and methine cellulose groups are visible at around
 274 2980-2830 cm⁻¹. Other characteristic bands related to the chemical structure of cellulose are the CH
 275 bending at 1315 cm⁻¹ (Wang, Fan, Gao, & Chen, 2006) and the absorption peak at 1159 cm⁻¹,
 276 attributed to C-O-C asymmetric stretching vibrations. With respect to the control fabric, the

277 infrared absorption bands of the treated samples show a decrease in the intensity of the broad band
 278 at $3600\text{--}3000\text{ cm}^{-1}$, indicating the presence of the coating on the cotton surface. In CO_B and
 279 CO_C spectra, the presence of the coatings is also confirmed by the peaks at 1732 cm^{-1} and 1174
 280 cm^{-1} attributed to the stretching modes of the ester bond carbonyl (C. Schramm, Binder, & Tessadri,
 281 2004) and to P=O, respectively. Since carboxyl groups contained on BTCA and PMIDA reacted
 282 both each other and also with the hydroxyl of cellulose chains, the ester absorption band on the
 283 cotton fabric results as the contribution of BTCA-cotton, PMIDA-cotton and BTCA-PMIDA ester
 284 linkages. Furthermore, some characteristic vibrations ascribed to --PO_3 moiety appear in the
 285 complex spectral region between $900\text{--}1200\text{ cm}^{-1}$ (Demadis, Armakola, Papathanasiou, Mezei, &
 286 Kirillov, 2014). Though this is a useful “fingerprint” region, the overlap with cellulose absorption
 287 bands makes them challenging to provide a full assignment. Finally, the sharp band at 812 cm^{-1} is
 288 attributed to the H-P-H wagging modes of sodium hypophosphite.



289
 290 **Fig. 2.** Normalized FT-IR spectra of CO_UT, CO_A, CO_B and CO_C.
 291

292 3.3. Thermal properties

293

294 In order to investigate the thermal and thermo-oxidative stabilities of treated and untreated
295 samples, TG and dTG analyses were carried out from 50°C to 700°C in both nitrogen and air
296 atmosphere, as shown in Fig. 3. In agreement with previous studies (Alongi, Camino, & Malucelli,
297 2013), the thermal degradation of cotton in nitrogen proceeds in one step, through two alternative
298 pathways that involve the depolymerization of cellulose units to volatile products (containing
299 levoglucosan, furan and furan derivatives) and the dehydration of the glycosyl units to char at
300 reduced temperatures. In nitrogen atmosphere, a maximum weight loss at about 360°C is observed
301 for the pristine cotton. The TG curves of the treated samples show a different behaviour: in fact, the
302 presence of the FR coatings is able to protect cotton from its degradation, exerting a thermal
303 shielding effect. In particular, with respect to the untreated cotton, the treated samples leave a
304 higher final residue and show a decrease in the temperature of maximum weight loss, regardless of
305 the number of deposited layers. The concomitant presence of P and N in the coating results useful
306 to prevent, at the same time, both the formation of volatile products during the first step of cellulose
307 decomposition and to enhance the formation of the char. In air atmosphere, all the treated samples
308 decompose following two steps, occurring at 200–400°C and 400–700°C. In fact, after a slight mass
309 loss at about 100°C, due to the evaporation of trapped moisture, the samples start decomposing at
310 around 270°C and show the maximum mass loss rate at around 320°C in first step, due to the
311 depolymerization of cellulose and the formation of aliphatic char. The scission of polymer chains,
312 followed by the formation of tars or low molecular weight products, like levoglucosan, which are
313 much more flammable than cellulose, can be observed. During the second step, the simultaneous
314 char oxidation and carbonization result in some aliphatic char that converts into an aromatic form,
315 producing CO and CO₂, with the maximum weight loss rate at around 500°C. The residues left at
316 the end of TG analyses (i.e. 700°C) for the treated samples are approximately 15 and 40 wt.% in
317 nitrogen and air atmosphere, respectively; conversely, the untreated cotton does not leave any

318 residue in air and below 5 wt.% in nitrogen. As compared to the untreated cotton, both in air and
319 nitrogen atmosphere, the TG and dTG curves of the FR treated fabrics (Fig. 3) show a remarkable
320 anticipation of the decomposition temperature and an increase of the residue at 700°C as well,
321 regardless of the presence of a sol-gel coating in both the second layers. In fact, in presence of
322 nitrogen-containing phosphorus-based coating, the fabrics show a reduced decomposition
323 temperature in the first step, which is attributable to the catalysed thermal dehydration of cellulose.

324 More specifically, when the treated samples are heated, the cellulose ester begins to pyrolyse
325 near 250°C, due to the formation of free phosphoric or polyphosphoric acid, able to react with the
326 crystalline regions at higher temperatures to form char and water. As a result, the thermal stability
327 of cotton could takes advantage from the anticipation of the first degradation step; besides, the
328 further decomposition of cotton at higher temperature is suppressed by the thermostable
329 carbonaceous structure, originated at lower temperatures due to the phosphorylation of C(6)
330 hydroxyl groups. The consequence is also visible in the second degradation step of the coated
331 fabrics, which is postponed with respect to the uncoated cotton, indicating the formation of a more
332 stable char at higher temperatures. The formed char protects the cellulosic substrate, hence reducing
333 the weight-loss percentage and rate during the first decomposition stage and shifting further
334 degradation towards higher temperatures, thanks to an enhanced aromatisation effect. Once again,
335 as already observed for the TGA carried out in N₂, the charring effect exerted by the flame retardant
336 treatments significantly increases the residues left at 700°C, which are about 15% higher than
337 untreated cotton, regardless of the coating composition.

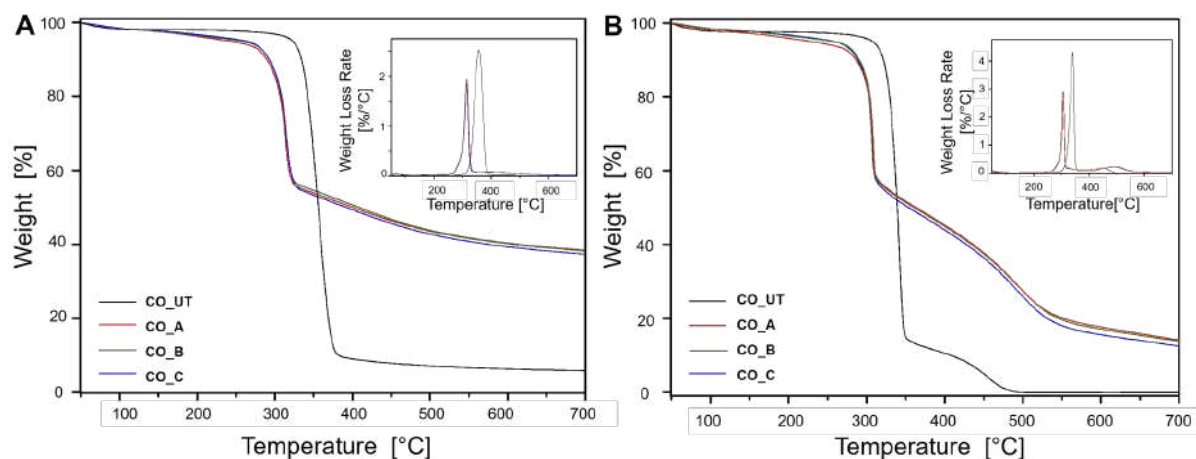


Fig. 3. TG and dTG curves in A) nitrogen and B) air atmospheres of CO_UT, CO_A, CO_B and CO_C samples.

3.4. Cone calorimetry tests

The combustion behaviour of treated and untreated cotton sample was investigated through cone calorimetry tests. From the collected data plotted and listed in Fig. 4, it is worth noticing that the presence of the coatings is able to dramatically reduce the combustion kinetics and the amount of total heat released during the combustion, as well as the production of smokes and its rate. Unlike the untreated sample, the treated fabrics, apart from an anticipation of the time to ignition (TTI, 24 s (CO_A), 24 s (CO_B), 18 (CO_C) vs. 2 s (CO_UT)), show a significant decrease of pkHRR and THR values (Fig. 4 A and B). In particular, the lowest pkHRR value is achieved for CO_B, the re-coated sample with a second APTES layer (129.88 kW/m²). On the contrary, the formulation containing GPTES and TEOS as second layer (CO_C) is not able to enhance the performances of nitrogen-containing carboxyl-functional organophosphorus finishing applied onto textile samples. It is not possible to clearly justify this finding, though the formation of cracks on the ceramic protective coating during the exposure to the heat flux could create preferential pathways for the heat and mass transfer, hence remarkably decreasing the FR performances in the forced combustion tests.

358 Furthermore, the presence of the FR coatings enhances the flame retardancy of cotton fabrics,
359 decreasing the combustion time, as confirmed by the Flame out values, as well as hindering the
360 formation of volatile species as evidenced by the strong decrease of the THR values. The
361 percentage of the residue is another parameter that reflects the incomplete combustion of the tested
362 samples: the mass loss of untreated cotton is 99%, higher than that of the treated fabrics (i.e. 81%
363 for CO_A, 80% for CO_B, 83% for CO_C).

364 Finally, the analysis of CO and CO₂, as the main components of fire gases, can provide useful
365 information on the mechanism of decomposition undergone by the cotton fabrics. According to the
366 literature (Nazaré, Kandola, & Horrocks, 2008), cellulose-based fabric produces CO and CO₂
367 during a two-step reaction: in the first step, during the pyrolysis reaction, carbon monoxide and
368 other gases are originated, while in the second step, when enough oxygen is available, carbon
369 dioxide is released due to the oxidation of CO.

370 Low CO₂/CO ratios suggest a limited conversion of CO to CO₂ as well as an inefficient
371 combustion. As regard to untreated cotton, the CO₂/CO ratio was 142.86. When cotton samples
372 were treated with FR finishing, the CO₂ production was a little lowered, leading to a noteworthy
373 decrease of CO₂/CO ratio (CO_A= 12.69; CO_B= 14.53; CO_C= 13.04). Finally, after cone
374 calorimetry tests, the residues of pristine cotton and of the treated fabrics appear completely
375 different (Figure 4C). In fact, the untreated sample left a tiny residue, while the finished fabrics
376 formed coherent and dense char, maintaining their original shape, notwithstanding a slight
377 shrinkage.

A	Sample	TTI (s)	Flame out (s)	pkHRR (kW/m ²)	THR (MJ/m ²)	Residue (%)	CO (%)	CO ₂ (%)	CO ₂ /CO
	CO_UT	43	75	154.2	3.9	1	0.0014	0.20	142.86
	CO_A	24	42	133.2	3.4	19	0.0134	0.17	12.69
	CO_B	24	44	129.9	3.3	20	0.0117	0.17	14.53
	CO_C	18	38	184.2	3.9	17	0.0138	0.18	13.04

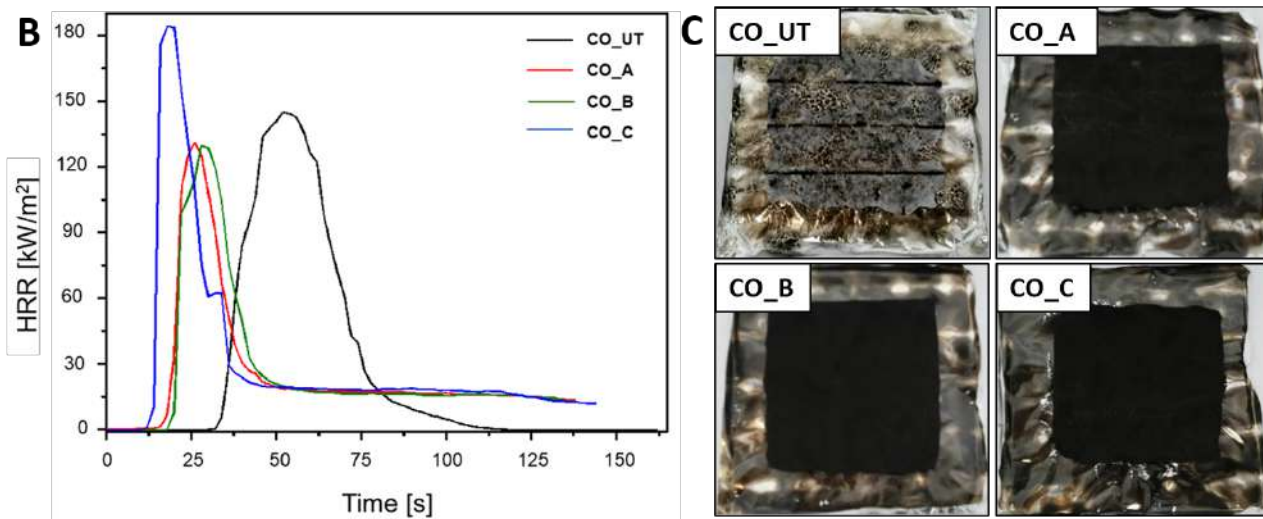


Fig. 4. A) Cone calorimetry data of untreated and treated samples; B) Heat release (HRR) curves for treated and untreated samples; C) Residues of tested samples from cone calorimetry tests performed at 35 kW/m².

3.5. Flammability tests

The flammability of the uncoated and coated cotton fabrics was investigated by horizontal and vertical flame spread tests. In general, comparing the two configurations, the kinetics in the horizontal test is slower and the total burning time is higher with respect to the vertical one, leading to a longer plateau in the flame transfer rate that permits a deeper differentiation among the types of tested samples.

The results and the images of the samples after burning with the respective afterflame time, afterglow time and residue (%) are summarized in Tables 3, for the horizontal and vertical

392 configurations. As it can be seen from the images, the original cotton fabric burns faster, leaving a
393 negligible residue. In horizontal configuration, immediately after ignition, on the untreated cotton a
394 vigorous flame appears, the duration of which is about 23 s, followed by a prolonged afterglow
395 (139 s); no residue could be found at the end of the test.

396 In contrast, when the cotton fabrics are treated by the designed FR coatings, a remarkable
397 modification in cotton flammability is observed, as the flame extinguishes immediately and narrow
398 chars are retained at the end of the tests. In details, by comparing the burning rates at t_1 (30 mm)
399 and t_2 (60 mm), the FR treated fabrics decrease their ignitability; furthermore, the final residue is
400 higher than that of untreated cotton (98.6%, 95.5% and 96.4% vs. 0%). In addition, the overall
401 damaged length of CO_A, CO_B and CO_C is between 5 and 20 mm. In good agreement with TG
402 data, these results further support the effectiveness of proposed FR formulations. Besides,
403 considering the Flammability Performance Index (FPI), CO_C shows better performances (19.28
404 %/s) than pure cotton (0%/s), CO_A (9.86%/s) and CO_B (6.37 %/s).

405 This is the demonstration that, as a consequence of the phosphorous treatment, which acts as a
406 flame retardant by limiting the degradation of cellulose, the silica coating is able to block the further
407 combustion of the polymer by creating a ceramic barrier onto the treated fabric surface.

408 Also in the vertical configuration, the untreated cotton fabric completely burns and is fully
409 consumed during the test, with 12 s of afterflame time and 10 s of afterglow time. Conversely, all
410 the treated samples completely stop the flame propagation, almost as soon as the flame is removed,
411 showing neither afterflame nor afterglow and reaching self-extinction.

412

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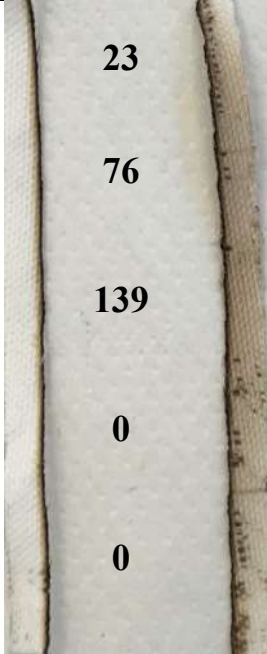
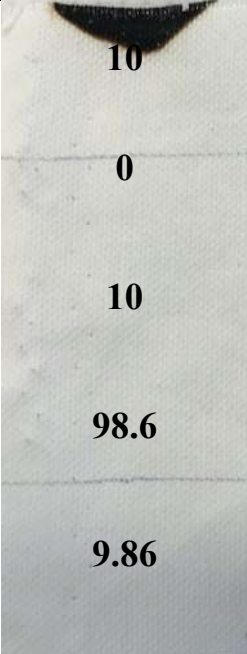
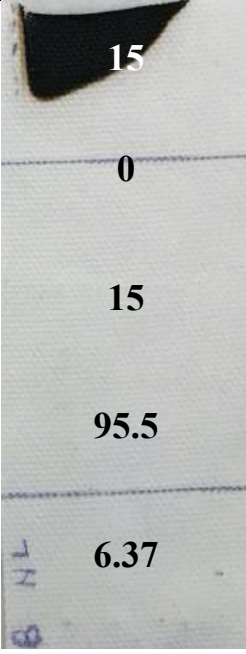
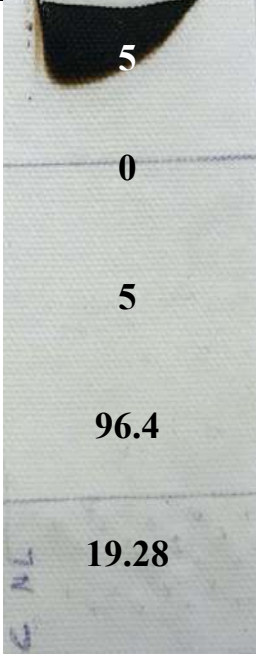




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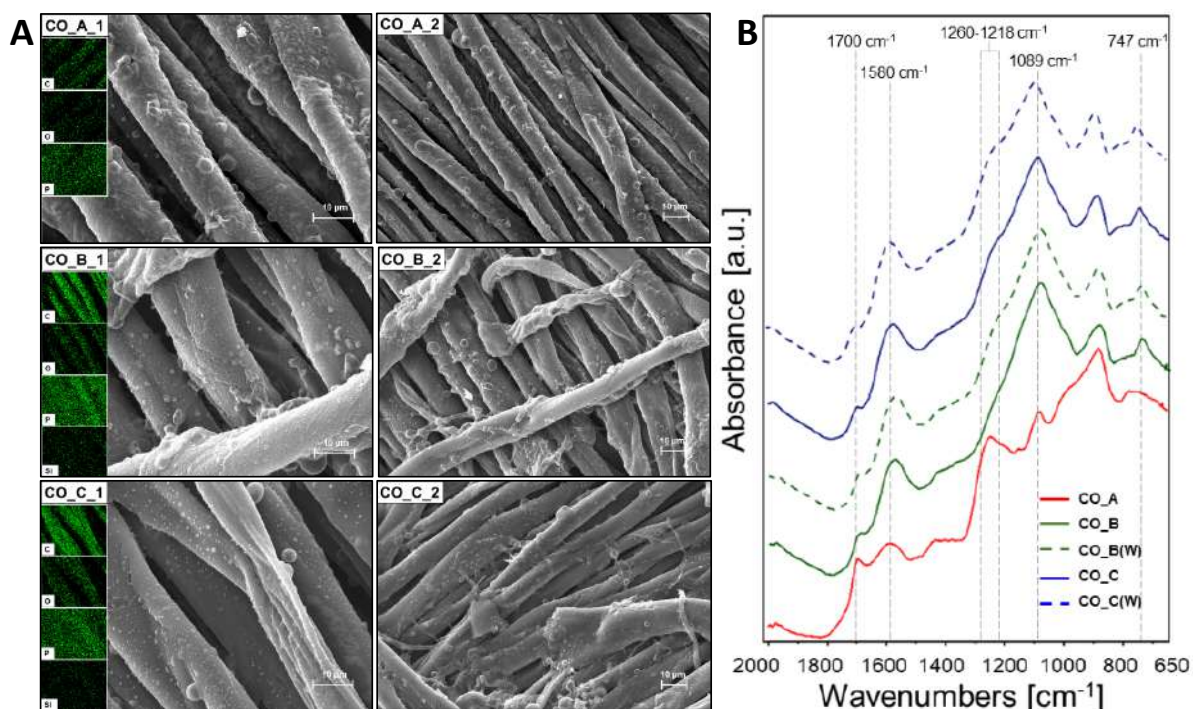
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Table 3.
 Results of the flame spread tests carried out in horizontal configuration CO_UT, CO_A, CO_B and CO_C unwashed samples.

Data	CO_UT	CO_A	CO_B	CO_C
Horizontal configuration				
	t ₁ (s)	23	10	15
	t ₂ (s)	76	0	0
	Total burning time (s)	139	10	15
	Residue (%)	0	98.6	95.5
	FPI (%/s)	0	9.86	6.37
Self-extinction	NO	YES	YES	YES
Vertical configuration				
	Self-extinction	NO	YES	YES

As shown in Fig. 5A, after the combustion, the texture of the cellulosic treated substrates is maintained thanks to the presence of FR treatment, which acts as a physical barrier inhibiting the transmission of energy, heat and O₂. In addition, as assessed through SEM_EDX analyses performed on the residues after flammability tests, the coated fabrics show the formation of

426 intumescent-like bubbles, mainly due to the release of phosphoric acid from the coating, which can
 427 phosphorylate cellulose, enhancing its dehydration and the consequent formation of a swollen char.
 428 As it can be seen from EDX mapping, the coating is still capable of creating a condensed charred
 429 residue containing carbon, oxygen and phosphorous elements, which are well-distributed
 430 throughout the burned areas.



432 **Fig. 5.** A) SEM images and elemental maps of the residues of CO_A, CO_B, CO_C at different
 433 magnifications (coded as _1 and _2, for x2.50 K and x1.00 K, respectively); B) ATR-FTIR of
 434 treated cotton fabrics pyrolyzed at 600°C, before and after one laundering cycle.

436 The thermal decomposition behaviour of the composites was characterized by TGA and FTIR
 437 analysis of char residues. As already highlighted, char residues play a significant role in improving
 438 flame retardancy of cotton fabric. To further elucidate their chemical structure, the residues left
 439 after flame spread tests were examined by FTIR analysis; the results are shown in Fig. 5B.
 440 Compared to unburned treated cotton fabrics, relative char residues show characteristic bands in the
 441 region 1700-650 cm⁻¹, according to the formation of unsaturated species. In fact, the peaks at
 442 around 1700 cm⁻¹ and 1580 cm⁻¹ can be assigned to C=O and C=C stretching modes, respectively.

443 In particular, the latter appears to be shifted with respect the band at 1600 cm^{-1} reported in the
444 literature, probably due to the more extended conjugation of C=C bonds. In addition, the
445 absorptions found in the region $1000\text{--}650\text{ cm}^{-1}$ may be due to the out of plane deformation
446 vibrations of the aromatic ring. Besides, the broad shoulder ranging from 1260 to 1218 cm^{-1} was
447 assigned to the stretching vibration of P=O and P-O-C, respectively. The FTIR spectra results
448 provide positive evidence that PMIDA produces phosphorous-based acids during thermal
449 degradation, which assisted, as dehydration agents, in the formation of the heat-resistant
450 carbonaceous char through carbonization process. The same results show that the cross-linking
451 reactions between PMIDA and cellulose-based fabric took place, giving rise to residues that well
452 protect the cotton substrates. The presence of the inorganic silica matrix results in the peaks at 1089
453 cm^{-1} and 747 cm^{-1} ascribed to the Si-O-Si stretching mode and to the Si-O-Si bending vibration. In
454 good agreement with results from TG and SEM analyses, FTIR investigation on the residues
455 confirms that the proposed coating has positive effects on char formation through the
456 depolymerization of cellulose (Soares, Camino, & Levchik, 1995).

457

458 3.6. Durability

459

460 In order to evaluate the durability of the proposed FR coatings, SEM and vertical flammability
461 tests were performed on the untreated cotton, as well as on the fabrics coated with a second layer
462 suitable for reacting with the free carboxylic groups onto FR treated textile samples. As previously
463 observed, as soon as it comes into contact with the flame, the untreated cotton fabric ignites
464 immediately and the flames quickly spread. Nonetheless, the treated samples burn slower than the
465 untreated one, leaving a coherent char structure at the end of the combustion. According to the
466 micrographs of washed samples (Figure 6A), confirming the leaching of most of the aggregates,
467 these results indicate that the fixation of FRs on cotton samples may not have been sufficient.

As shown in Table 4, at the end of the tests, with respect to the unwashed textiles, laundered re-coated FR fabrics still leave a significant and compact residue that is around 50% for both CO_B and CO_C samples; these latter look well covered by the coatings containing C, O, P and Si elements, as confirmed by elemental analysis.

Table 4.

Results of the flame spread tests carried out in horizontal configuration for CO_UT, CO_B and CO_C washed samples.

Data	CO_UT	CO_B_W	CO_C_W
t ₁ (s)	23	27	24
t ₂ (s)	76	110	95
Total burning time (s)	139	165	161
Residue (%)	0	52.2	50
Self-extinction	NO	NO	NO

The substrate texture appears still visible; however, as far as the flammability resistance of the specimens is concerned, the laundered fabrics lower their classification from self-extinguishing to flame retardant. Evidently, calcium ions in the water are able to bind the unreacted hydroxyl groups of both polycarboxylic and organophosphorus acids linked to the cellulose, hence forming insoluble salts that inhibit the flame retardant performance of the applied coatings.

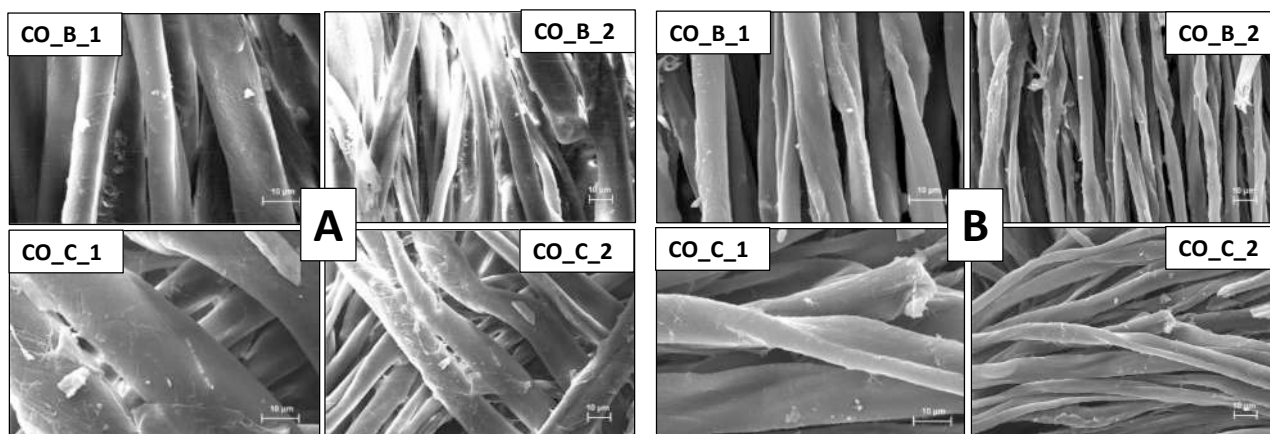


Fig. 6. SEM images of A) washed CO_B and CO_C samples at different magnifications (coded as _1 and _2 for x2.50 K and x1.00 K, respectively) and B) residues of washed CO_B and CO_C samples at different magnifications, (coded as _1, _2, for x2.50 K, x1.00 K, respectively).

After flame spread tests, also the residues of the washed fabrics were investigated by SEM. Two different magnifications are shown in Fig. 6B: it is noteworthy that the charred residues are still able to preserve the texture of the pristine cellulosic substrate.

4. Conclusions

The global request for less toxic products has increased the demand for fire retardant treatments that should be effective in the protection of textile fabrics, as well as safe for humans. In this work, the FR effectiveness of a nitrogen-containing phosphorous based compound to cotton fabrics was investigated mainly in combination with TEA, BTCA and its phosphorus-based catalyst (i.e. sodium hypophosphite). The main advantages of the proposed FR finishing refer to its eco-friendliness, since it does not contain halogen-based molecules and does not release formaldehyde, which is the worst problem in the use of commercially available additives based on N-methylol compounds. With respect to the untreated cotton, an increase in flame retardant performances of the treated fabrics was observed, with a reduction of both the total burning time and rate, as well as

503 with a higher char amount left at the end of combustion. These data suggest that the proposed FR
504 multilayer coatings could effectively control the combustion process and favour the achievement of
505 self-extinction for the treated fabrics. Unfortunately, the flame spread tests performed on washed
506 treated samples suggest a partial leaching of the FR coatings from cotton surfaces, though the
507 residual char of the coated fabrics still perfectly maintains the textile texture, due to the protective
508 effect exerted by the remained coatings. The attempt to bind the BTCA free carboxylic acid groups
509 to the cotton fabric by sol-gel based coatings was not successful. Further investigations are
510 underway to design FR coatings with high washing fastness.

511

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