1   **Vinylphosphonic acid/methacrylamide system as durable intumescent flame retardant for**

2   **cotton fabric**

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12

13   **Abstract**

14   A novel intumescent flame retardant treatment, consisting of vinylphosphonic acid (VPA) as the

15   acid source and methacrylamide (MAA) as blowing agent, was designed and applied onto cotton

16   fabrics. The grafting of reactive monomers onto cellulose chains was carried out using potassium

17   persulfate as initiator of a radical polymerization technique. The thermal and fire behavior of the

18   treated fabrics was thoroughly investigated: in particular, the VPA/MAA coating was able to exert a

19   protective action, giving rise to the formation of a stable swollen char on the surface of textile fibers

20   upon heating, hence improving the flame retardancy of cotton. In addition, the treated fabric

21   achieved self-extinction as assessed by horizontal flame spread tests. Finally, a remarkable weight

22   loss was observed only after the first washing cycle, then the samples did not show any significant

23   weight loss, hence confirming the durability of the self-extinguishing treatment, even after five

24   laundering cycles.

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**Introduction**

The massive use of cellulose-based materials in our everyday life is driven by their remarkable combination of properties and in connection with the growing range of application fields. As main component of cotton, cellulose is used to produce apparel, home furnishings and industrial products, despite its easy flammability, as confirmed by low limiting oxygen index (LOI about 19%) and combustion temperature (360-425°C) (Wakelyn et al. 2007). In fact, when ignited, cotton fibers burn rapidly and the flame spreads quickly, causing several problems such as loss of material properties, production of gases and smoke during combustion, which could affect both human life and equipments (Li et al. 2010). In recent years, in many industrialized countries, such as Austria, Spain, Netherlands, United Kingdom and United States, the death rates caused by fire have been consistently reduced (Rohde et al. 2016). Despite all, there is a high degree of variation among different countries and the data are not fully encouraging. In 2015, there were 1,345,500 fires reported in the United States, which caused 3,280 civilian deaths, 15,700 civilian injuries, and $14.3 billion in property damage ("http://www.nfpa.org/news-and-research/fire-statistics-and-reports/fire-statistics/fires-in-the-us,"). Consequently, improving the fire retardant behavior of cotton by using various flame retardants, able to inhibit ignition and to slow down the burning rate or to modify the combustion mechanism, is a major challenge for decreasing mortality for burn injuries and extending the fabric use to several technical applications (Liao and Rossignol 2000). The most important approach to flame retardant finishes was set between 1950 and 1980, in the well-known "Golden period" of fire retardants (Horrocks, 2011), started after the success of those developed in the Second World War. Afterwards, little research was developed during the period from 1980 up to

2000 due to the environmental issues that some flame-retardants were showing. Currently, legislatives measures like REACH (Registration, Evaluation, Authorization and Restriction of Chemical substances) Act and the Detox initiative promoted by Greenpeace organization are limiting the use of bromine containing flame retardants for their proven or suspected adverse effects on the environment. This has led to extensive research into the area of flame retardants for textile fabrics, accelerating the development of halogen-free alternatives (Anna et al. 2002; "Environmental Health Criteria 192 Flame Retardants: a General Introduction," 1997; Laoutid et al. 2009). Therefore, in the last years, new products and bio-sustainable treatments to improve flame retardancy in textile fabrics attracted a great interest from academic research (Horrocks, 2011; Horrocks, 2003; Horrocks, 1986; Bourbigot, 2008; Weil and Levchik 2008; Alongi et al. 2014a; Salmeia et al. 2016). Among the environmentally friendly flame retardant systems reported in literature, the use of nanoclays (Alongi et al. 2012a; 2014c) and phosphorous compounds is well established (Ebdon et al. 2000). In particular, this latter class of flame retardants comprises either inorganic or organic structures, notwithstanding that elemental P can be exploited as well (Lu and Hamerton 2002): they can act in the vapor phase or in the condensed phase, and sometimes can operate simultaneously in both phases (Aseeva and Zaikov 1985). Recently, to improve flame resistance of cotton fabrics, phosphorous-based chemicals were employed in sol-gel method, due to the possibility of this technique to be modified easily in the sol stage by chemical or physical interactions with other functional materials (Brancatelli et al. 2011). Cotton finishing by sol-gel method to improve flame retardancy has been systematically studied (Alongi and Malucelli 2012; Vasiljević et al., 2013; Kappes et al. 2016), also aiming at investigating the synergism among silica, nitrogen and phosphorus in the thermal behaviour (Alongi et al. 2014b; 2013), within the development of intumescent systems (IS). In presence of cellulose, i.e. a carbon rich polyhydric material, the major components typically required to design IS are an acid source and a blowing agent. The former, during the pyrolysis, releases an acid able to catalyze cellulose dehydration as a

76    char promoter and to form an insulating carbonaceous layer between the polymer and flame. The

77    latter is a low-temperature boiling chemical, often a nitrogen compound, which releases inert gas

78    when exposed to high temperatures, leading to the swelling of the polymer and to the formation of a

79    swollen multicellular layer. Recently, PVA has been investigated in order to improve both flame

80    resistance and multifunctionality in cotton fabrics (Parvinzadeh Gashti and Almasian 2013;

81    Nooralian et al. 2016).

82    To the best of our knowledge, no studies have investigated the thermal behaviour of cotton fabric

83    finished by vinylphosphonic acid and methacrylamide as source of phosphorous and nitrogen,

84    respectively, with the aim to develop an intumescent cellulose treatment. These vinyl monomers

85    containing phosphorus and nitrogen are great potential candidates for the flame retardant

86    modification of cotton fabric due to the key role of P-N synergism in flame retardancy. The

87    objective of this study is to characterize the efficacy of flame retardant coating obtained by graft

88    copolymerization of the above-mentioned monomers, initiated by potassium persulfate, onto cotton

89    fabric. Scanning Electron Microscopy (SEM), coupled to Energy Dispersive X-ray (EDX) analysis,

90    FT-IR spectroscopy and weight percentage changes between treated and untreated samples have

91    been used to investigate the morphology, the surface composition and the coating durability. The

92    thermal and thermo-oxidative stability of the treated fabrics have been assessed by

93    thermogravimetric analyses in nitrogen and air and compared with untreated cotton. Furthermore,

94    horizontal flame spread and cone calorimetry tests have been exploited for evaluating the flame

95    retardant features of the obtained materials; these tests have also been repeated after one and five

96    standardized washing cycles, in order to check the stability and durability of the proposed chemical

97    grafting.

98

99    **Experimental part**

100

4

Materials

Vinylphosphonic acid (97%) (VPA), methacrylamide (98%) (MAA) and potassium persulfate (KPS) were purchased from Sigma-Aldrich and used without further purification. The grafting was carried out on a scoured and bleached 100% plain-weave cotton fabric (mass per unit area of 237 g/m$^2$). The textile samples were washed in a non-ionic detergent at 40°C for 20 min, operating at about pH = 7. Finally, the fabrics were rinsed several times with de-ionized water, dried and put into drier for storage. Prior to all the experiments, the cleaned samples were conditioned under standard atmospheric pressure at 65 ± 2% relative humidity and 20 ± 1 °C for at least 24 h.

Method

Experimental conditions were based on preliminary studies developed in our laboratory, which assessed their effectiveness for cotton grafting using selected vinyl monomers, in order to produce the thinnest film with the highest flame resistance. VPA (13.94 g, 0.129 mol) was dissolved in 14.5 ml of de-ionized water into a three-round bottom flask equipped with a thermometer and fluxed with nitrogen during the whole experiment, aiming at reducing dissolved oxygen that could inhibit the graft polymerization. The solution, under vigorous stirring, was adjusted to pH 3.5 with NaOH and then heated to 60°C. MAA (10.97 g, 0.129 mol) was dissolved in 15 ml of de-ionized water at 60°C under vigorous stirring and then it was slowly added to the VPA solution. After 10 minutes, KPS as initiator of graft polymerization was added to the obtained solution (2.53 g, 10% w/owm (on weight of both monomers)) at 60°C under stirring. Preliminary studies were conducted to identify application key parameters to allow the cotton grafting process inhibiting, at the same time, gelation phenomena. More specifically, to avoid any premature gelation during the preparation step, the clear solution containing VPA/MAA/KPS was applied on cotton fabrics within 10 min at 60°C,

through a two-roll laboratory padder (Werner Mathis, Zurich, Switzerland), using 2 bar nip pressure. Samples were dried for 20 minutes at 60°C and then cured at 165°C for 3 minutes in an electric laboratory oven. To evaluate the durability of the coating, washing fastness has been assessed up to 5 washing cycles using a Labomat Mathis equipment (Werner Mathis AG), according to the international standard EN ISO 6330:2000.

The total dry solids add-on (A, wt.%) on cotton sample and the weight loss of the coating after washing cycles (WLW, wt. %), were calculated using a Mettler balance ($10^{-4}$ g) according to Eq.1 and Eq.2 respectively:

$$A = \frac{W_T - W_{UT}}{W_{UT}} \times 100 \tag{1}$$

$$WLW = \frac{W_{TW} - W_T}{W_T} \times 100 \tag{2}$$

where $W_{UT}$ and $W_T$ are the dry weights of the cotton samples before and after the pad-cure treatment respectively, while $W_{TW}$ is the dry weight of the cotton sample after washing cycles. Textile fabrics, before and after the washing cycles, were weighted five times with the standard deviation always lower than 2%. The final dry add-on of the treated sample was 67.4%, while its weight losses after 1 and 5 washing cycles were 34.2 and 34.6% respectively.


Characterization techniques


FT-IR spectra were recorded at room temperature in the range from 4000 to 650 cm$^{-1}$ with 32 scans and a resolution of 4 cm$^{-1}$ using Thermo Avatar 370 spectrophotometer, equipped with attenuated total reflection (ATR) accessory using a diamond crystal. The collected spectra were normalized to the band at 1314.8 cm$^{-1}$ (CH$_2$ wagging of cellulose), which falls in a region where the absorption bands attributable to the vinyl graft film are not present.

149  The surface morphology of the treated samples was studied using a LEO-1450VP Scanning

150  Electron Microscope (beam voltage: 5 kV), equipped with an X-ray probe (INCA Energy Oxford,

151  Cu-Ka X-ray source, $k\alpha$ = 1.540562 Å), which was used for performing the elemental analysis.

152  Treated and untreated fabric samples (0.5 cm x 0.5 cm) were cut and fixed to conductive adhesive

153  tapes and gold-metallized.

154  The thermal stability of the fabrics was evaluated by thermogravimetric (TG) analyses, both in

155  nitrogen and in air (60 mL/min), from 50 to 800 °C with a heating rate of 10 °C/min. The samples

156  were placed in open alumina pans (ca. 10 mg), using a TAQ500 thermogravimetric balance. The

157  experimental error was ±1°C on the temperature and ±0.5% on the weight.

158  In order to evaluate the flame retardant properties of the cotton samples, horizontal flame spread

159  tests were carried out by applying a methane flame (25 mm long) for 3 s to the short side of the

160  samples (50 mm x 100 mm), which were clamped to a U-shaped metallic frame tilted 45° with

161  respect to the plane. The tests were repeated four times for each formulation in order to get

162  reproducible data. Relevant parameters such as burning time, rate and final residue were measured.

163  The combustion behaviour of square fabric samples (50 mm x 50 mm) was investigated using a Fire

164  Testing Technology cone calorimeter (according to ISO 5660). The measurements were carried out

165  using a heat flux of 35 kW/m$^2$ in horizontal configuration, following the procedure described

166  elsewhere (Guido et al. 2013). Time to ignition (TTI, s), peak of heat release rate (pkHRR, kW/m$^2$),

167  total heat release (THR, kW/m$^2$) and final residue (R %) were measured. With the aim to ensure

168  reproducible and significant data, the experiments were repeated four times for each material

169  investigated, leading to an experimental error of 5 %. Prior to flammability and combustion tests, all

170  the specimens were conditioned at 23 ± 1°C for 48 h at 50 % R.H. in a climatic chamber. The

171  samples were coded as follows: CO_UT (untreated cotton), CO_T (treated cotton), CO_T1W

172  (treated cotton after 1 washing cycle) and CO_T5W (treated cotton after 5 washing cycle).

173

**Results and discussion**

Graft polymerization

Vinyl graft copolymerization of cellulose-based polymer represents a useful way to modify the surface of cotton fabric, as well as to widen the applications of this latter. As a low cost alternative of other initiators, in this study we used KPS catalyst in aqueous medium. In fact, this catalyst is one of the most engaging initiators of graft vinyl monomers on macromolecule bearing oxidizable functional groups, in which free radicals are generated on polymer chains.

The basic mechanism is commonly referred to as a "grafting from" (Jenkins and Hudson 2001) and starts from the creation of free radical sites on the cellulose polymer chain, whereby both the vinyl monomers used can react with the radicals to propagate onto the surface, in order to obtain a permanent combination of VPA and MAA onto the cellulosic substrate. As a consequence of grafting process, covalent bonds are formed between monomers and polymers, hence providing new functionalities to the treated fabric with high durability. As reported in the scientific literature (Khalil et al. 1993), the decomposition of persulfate ions due to heating of its aqueous solution allows the formation of sulfate ion-radicals ($SO_4^{-\bullet}$) able to react with water molecules to produce $OH^{\bullet}$ radicals as described by equations (a) and (b) in Scheme 1. Both free radicals attack the double bond of vinyl monomers in solution thereby producing other radicals (eq. (c) and (d)), able to initiate reactions of homo and co-polymerization (Rosace and Massafra 2008). During this step in aqueous solution, the formed radical initiator can allow the formation of branched structures resulting in three-dimensional insoluble network characterized by a large molecular weight: this outcome is known as Trommsdorff-Norrish effect, in contrast to the formation of soluble molecules with defined molecular weight (Zhu and Hamielec 1993; Carlsson et al. 2010). According to the

198 preliminary studies to minimize the above-mentioned gelation phenomena, the cotton fabric was

199 rapidly treated with the finishing solution.

200 Once cotton fabrics are wetted, free radical species can attack the textile polymer producing macro-

201 radicals by direct abstraction of hydrogen atoms from the cellulose molecules and then initiating

202 grafting reactions onto polymer surface (Eq. (e)-(g)). Afterwards, propagation reactions take place

203 increasing the graft polymerization between vinyl monomers and cellulose macroradicals (Eq. (h)-

204 (k)). Finally, termination of grafting reactions onto cellulose chain can occur by a reaction with the

205 initiator, coupling or disproportionation (Rosace and Massafra 2008). These reactions determine the

206 formation of P- and N- doped polymer chains covalently bonded with the cotton surface.

207

208 **Scheme 1**

209

210 In order to confirm the successful graft co-polymerization of vinyl monomers onto carbohydrate

211 chains and the variation in the characteristic absorption bands of cotton (Chung et al. 2004; Gürdağ

212 and Sarmad 2013), FTIR spectra of treated and untreated samples were carried out; the results are

213 shown in Fig. 1. With respect to the control fabric, the infrared absorption bands of the treated

214 sample in the ranges 3500–3000 cm$^{-1}$ and 3000–2800 cm$^{-1}$, characteristic of hydrogen bonded O-H

215 stretching and C-H stretching of cellulose, respectively, decrease in the intensity due to the presence

216 of the vinyl based film on the surface of the treated cotton fabric. The disappearance of the

217 characteristic absorption band assigned to C=C at 1614 cm$^{-1}$ and 1646 cm$^{-1}$ for vinyl groups of VPA

218 and MAA, respectively, confirms the graft co-polymerization of both vinyl monomers onto cotton

219 fabric. The presence of MAA is further confirmed by the appearance of absorption bands

220 characteristic of the amide group and assigned to C=O stretching (1657 cm$^{-1}$) and NH$_2$ bending

221 (1599 cm$^{-1}$). In addition, the FT-IR band at 1402 cm$^{-1}$ is ascribed to the C-N stretching, while the

signal at 760 cm$^{-1}$ is assigned to the N-H out-of-plane bonding (El-Hady and Ibrahim 2004; Lanthong et al. 2006; Kumar et al. 2009). Furthermore, the peaks at 1260 cm$^{-1}$ and 1455 cm$^{-1}$ are attributable to P=O stretching and CH out-of-plane bending, respectively (Bantchev et al. 2016; Alongi et al. 2012c; Edwards et al. 1993). In particular, the latest peak appears clearly increased with respect to the existing absorption band of the cellulose chain due to the contribution of both monomers. Finally, the obtained modification of cotton fabric is confirmed by the variation of its absorption bands in the range 1000-1054 cm$^{-1}$, partially overlapped by VPA peaks between 1000 and 1046 cm$^{-1}$ (Yildiz et al. 2016). The durability of the coating was also evaluated through FT-IR spectroscopy, monitoring the characteristic bands of the graft co-polymerized cotton fabric before and after washing cycles. The decrease in intensity of the absorption bands previously described and related to VPA and MAA confirm the occurrence of a partial weight loss of the treated sample after 1 washing cycle. This finding is further verified by the increase of the characteristic peaks referring to the pristine cotton fabric, due to the partial loss of non-grafted vinyl-based film. It is worthy to note that the treated fabrics lose weight only after the first washing cycle, with a negligible further weight loss after five launderings, hence confirming the durability of the proposed treatments; furthermore, the FTIR spectra acquired after 5 washing cycles are practically overlapped to those obtained after the first washing cycle.

**Figure 1**

In addition, the removal of the copolymer clusters not grafted on the cotton surface allows the treated fabric to recover its initial touch sensation (i.e. "fabric hand).

Morphology

10

247    In order to investigate evidence of any relevant change in the fabric surface due to the deposition of

248    the vinyl based film coating, scanning electron microscopy (SEM) analyses were performed; some

249    typical images, at different decreasing magnifications, for treated (both washed and unwashed) and

250    untreated cotton fabrics are shown in Fig. 2. The images of unwashed treated cotton fabric (CO_T)

251    show an inhomogeneous coating in individual yarns of fabric; in particular, several clusters (in the

252    range of 1-10 μm) appear clearly on the fiber surface. They are probably due to the occurrence of

253    co-polymerization reactions between the monomers, which are not grafted on the cotton surface. In

254    fact, the same aggregates disappear in the SEM image of the washed treated sample (CO_T1W),

255    due to the removal of the aforementioned clusters by the washing medium. Subsequently to the

256    washing cycle, a homogeneous and compact film uniformly distributed onto the textile fibers

257    appears. This finding was confirmed even after 5 washing cycles.

258

259                                              **Figure 2**

260

261    The composition of the films was semi-quantitative evaluated by energy dispersive X-ray analysis

262    (EDX). As shown in Fig. 3, for treated cotton fabric surfaces, phosphorus was the only detected

263    element in addition to the fabric reference, due to the presence of C and O peaks, which are very

264    close each other, hence hindering that of nitrogen (Alongi et al. 2012b; 2011).

265

266                                              **Figure 3**

267

268    Thermal and thermo-oxidative stability

269

270 The thermal and thermo-oxidative stability of the pure and treated cotton fabrics has been assessed

271 by thermogravimetric analyses performed in nitrogen and air, respectively. Tables 1 collects the

272 obtained data for the different materials investigated. TG and dTG curves of all samples in both air

273 and nitrogen atmosphere, are plotted in Fig. 4.

274

275 **Figure 4**

276

277 As clearly reviewed in the scientific literature, the thermal degradation of cellulose starts at 300–

278 400°C, according to two competitive pathways, i.e. dehydration and depolymerization. The former

279 is initiated by the scission of acetal bonds between the chain glycosidic units and goes through the

280 splitting, from the resultant chain ends, of a volatile cyclic monomer of cellulose, i.e. levoglucosan.

281 Competing dehydration reactions favor the formation of thermally stable aliphatic structures (char

282 I), which successively convert into aromatic structures (char II), together with the production of

283 water, methane, carbon monoxide and carbon dioxide (400–600°C). The aromatic structures of char

284 II (ca. 18%) are thermally stable at least up to 800°C (Alongi and Malucelli 2015; Horrocks 2001;

285 Low and Morterra 1985; Morterra and Low 1985; Morterra et al. 1984; Price et al. 1997;

286 Shafizadeh and Bradbury 1979).

287 In nitrogen, upon heating, cotton fabrics start to degrade at about 336°C ($T_{onset10\%}$, Table 1), losing

288 10 % wt.; then the fabric further goes on degrading, achieving a maximum weight loss rate at about

289 362°C ($T_{max1}$) that corresponds to 49.7% weight loss. Then, only in the case of the treated fabrics, a

290 second maximum weight loss peak appears in the derivative (dTG) curves within 411 and 419°C:

291 this degradation step is likely to be ascribed to the degradation phenomena involving both the

292 coating components and the char formed at lower temperatures.

293 The presence of the intumescent coating significantly anticipates the cellulose decomposition: in

294 particular, regardless of the possible washing cycle applied to the treated fabrics, $T_{onset10\%}$ and $T_{max1}$

12

values decrease, while, at the same time, the residues found at $T_{max1}$ are within 63 and 72%. This finding can be attributed to the presence of vinylphosphonic acid that, upon activation, favors the cellulose decomposition towards dehydration, hence limiting the production of volatile species and giving rise to the formation of a protective and quite stable char, as indicated by the high residues found at $T_{max1}$ by comparing the values listed in Table 1. Furthermore, the protective effect exerted by the applied coating is also demonstrated by the remarkable increase of the residues at 700°C. By further comparing the thermogravimetric data of the treated fabrics, before and after washing, it is worthy to note that this latter seems to slightly worsen the thermal stability of the cellulosic substrate: in fact, after washing (CO_T1W sample), the residues at $T_{max1}$, $T_{max2}$ and at 700°C are lower as compared to CO_T counterpart. Furthermore, no significant difference was detected on the sample after 5 washing cycles, confirming the result obtained by FT-IR and SEM characterization: once the film not grafted onto the fabric comes off, the coating is able to withstand the laundering cycles.

In air (Table 1), the thermo-oxidation of cellulose proceeds in a similar way, which differs from the degradation in nitrogen just for the presence of a second degradation step at high temperatures ($T_{max2}$: 471°C). This phenomenon can be ascribed to the oxidation of the char formed during the first step and of all the hydrocarbon species still present.


**Table 1**


Once again, the deposited coating is responsible for an anticipation of the degradation of the fabric, i.e. for the decrease of both $T_{onset10\%}$, $T_{max1}$ and $T_{max2}$, as well as for the increase of the residues at $T_{max1}$, $T_{max2}$ and 700°C that confirm the protective effect exerted by the formed stable char. Besides, the washing cycles applied to the treated fabrics shows a detrimental effect as far as the formation of a stable char is considered: in fact, despite a slight increase of $T_{max1}$ and $T_{max2}$ values, the

residues at these two temperatures and at 700°C remarkably decrease after washing (63.2, 44.3, 34.3 wt.%, respectively), notwithstanding that they are still much higher than those of the untreated cotton.

Flammability tests

All the treated and washed fabric samples were subjected to horizontal flame spread tests, according to UL94 HB standard. These tests have already been exploited in several previous works for assessing the flammability behavior of textiles (Casale et al. 2016; Grancaric et al. 2015; Alongi et al. 2014a). Table 2 summarizes the flammability results. The untreated fabric samples (CO_UT) burn completely with a final glowing combustion (GC), and a negligible residue (Table 2).

**Table 2**

Conversely, the treated fabric samples, either before or after the washing cycles, achieve self-extinction few seconds after the flame application. It is worth noticing that even 5 washing cycles did not change the flammability behavior of the treated fabrics, which achieved self-extinction similarly to those subjected to one washing cycle only. As already pointed out in the discussion of thermogravimetric data, this finding can be ascribed to the presence of the coating on the fiber surface, which favors the dehydration of the fabric, releasing water and ammonia, which results in an enhanced fire retardant effectiveness. Even the small portion of burnt textile still shows its texture and is mechanically resistant and coherent.

Referring to the morphology of the treated fabrics after the horizontal flame spread tests, the intumescent-like behavior of the applied coating is clearly shown in the SEM pictures collected in Fig. 5: in particular, upon exposure to a flame, the coatings swells and give rise to the formation of

345  bubbles on the burnt surfaces. It is worth noting that, after the washing cycle, the intumescent

346  behavior is significantly reduced, probably because of the removal of the applied coating not

347  grafted to the fabric surface, although the washed fabrics still achieve self-extinction.

348

349  **Figure 5**

350

351  Finally, the results of the elemental analyses performed on the residues after flammability tests still

352  indicate the presence of phosphorus element, homogeneously distributed on the fibers and in the

353  fabric interstices: as an example, Fig. 6 shows the mapping of C, O and P elements for CO_T1W

354  residue after flammability tests.

355

356  **Figure 6**

357

358  Cone calorimetry tests

359

360  Cone calorimetry tests have been carried out in order to assess the reaction and efficiency of the

361  designed coating upon exposure to a heat flux (35 kW/m$^2$). Table 3 collects the obtained data, in

362  terms of Time To Ignition, Total Heat Release, peak of Heat Release Rate and final residue.

363  Under a 35 kW/m$^2$ heat flux, cotton burns vigorously in 160 s, while the coated fabric does not

364  ignite at all; in fact, this sample undergoes thermal-oxidation, leaving a 31 wt.% final residue,

365  which is still coherent and consistent. By this way, the treated fabrics undergo pyrolysis, instead of

366  combustion. Some images of the residues after cone calorimetry tests are shown in Table 3. Finally,

367  it is worthy to note that the treated fabrics, despite a significant decrease of the final residue (13 vs.

368  31 wt.%, before and after washing, respectively), still do not ignite even after performing the first

washing cycle or even after 5 washing cycles: this finding further confirms the durability and protection exerted by the applied coating.


**Table 3**


**Conclusions**


In this study, a combination of vinyl monomers (vinylphosphonic acid and methacrylamide), in the presence of KPS as radical-initiator, was used to allow a permanent chemical modification of cotton surface. The results showed that the VPA-MAA coating is able to enhance the thermal and thermo-oxidative stability of cotton, confirming the char-forming and intumescent effect exerted by the phosphoric acid source and by the nitrogen present in MAA. The chemically modified textiles showed high levels of flame retardant performance and self-extinguished in horizontal flame spread tests. Therefore, this new halogen-free flame retardant finishing, durable and effective at least up to five washing cycle, may represent a valid alternative to the commercially available treatments for cellulose-based polymers.


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**Captions**

514    **Scheme 1** Schematic representation of graft initiation and propagation of radical reactions

515

516    **Fig. 1** FT-IR spectra normalized of CO_UT, CO_T, CO_T1W and CO_T5W

517

518    **Fig. 2** SEM images of CO_UT, CO_T and CO_T1W at different magnifications, coded as: _1, _2,

519    _3 for 2.50 K X, 1.00 K X and 250 X, respectively

520

521    **Fig. 3** Elemental analyses of CO_UT, CO_T and CO_T1W

522

523    **Fig. 4** TG and dTG curves in nitrogen (A) and air (B) atmospheres of CO_UT, CO_T and CO_T1W

524    samples

525

526    **Fig. 5** SEM images of CO_T and CO_T1W residues after flammability test at different

527    magnifications, coded as: _1, _2, _3 for 2.50 K X, 1.00 K X and 250 X, respectively

528

529    **Fig. 6** Elemental analyses of CO_T1W residue after horizontal flame spread tests

## SCHEME 1.

Graft initiation in solution

$$S_2O_8^{2-} \xrightarrow{\text{heating}} 2SO_4^{-\bullet} \tag{a}$$

$$SO_4^{-\bullet} + H_2O \longrightarrow HSO_4^- + OH^\bullet \tag{b}$$

$$\left(R^\bullet = SO_4^{-\bullet},\ OH^\bullet\right)$$

$$R^\bullet + \text{(CH}_2\text{=CH–PO(OH)}_2) \longrightarrow R\text{–CH}_2\text{–}\overset{\bullet}{\text{CH}}\text{–PO(OH)}_2 \tag{c}$$

$$R^\bullet + \text{(CH}_2\text{=C(CH}_3\text{)CONH}_2) \longrightarrow R\text{–CH}_2\text{–}\overset{\bullet}{\text{C}}(\text{CH}_3)\text{CONH}_2 \tag{d}$$
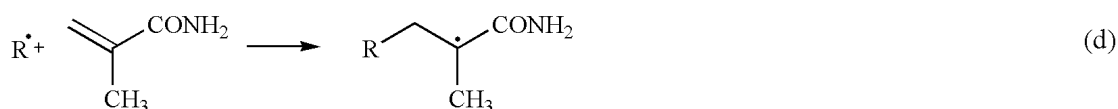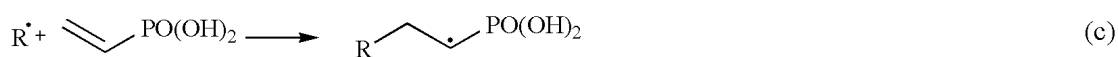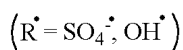
Graft initiation on cotton fabric

$$R^\bullet + \text{CELL—OH} \longrightarrow \text{CELL—}\overset{\bullet}{\text{O}} + RH \tag{e}$$

$$\text{CELL—}\overset{\bullet}{\text{O}} + \text{(CH}_2\text{=CH–PO(OH)}_2) \longrightarrow \text{CELL–O–CH}_2\text{–}\overset{\bullet}{\text{CH}}\text{–PO(OH)}_2 \tag{f}$$

$$\text{CELL—}\overset{\bullet}{\text{O}} + \text{(CH}_2\text{=C(CH}_3\text{)CONH}_2) \longrightarrow \text{CELL–O–CH}_2\text{–}\overset{\bullet}{\text{C}}(\text{CH}_3)\text{CONH}_2 \tag{g}$$
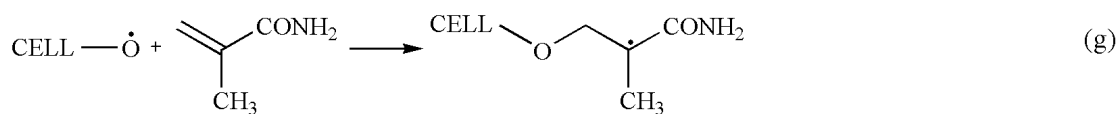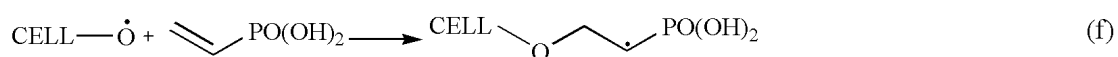
Graft propagation on cotton fabric



(h)

(i)

(j)

(k)
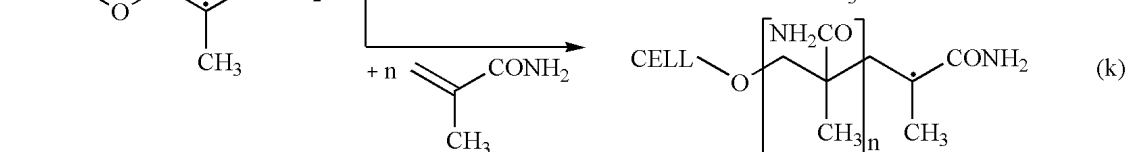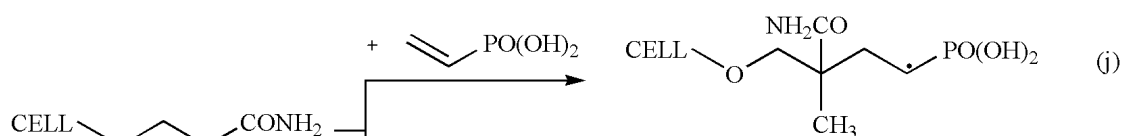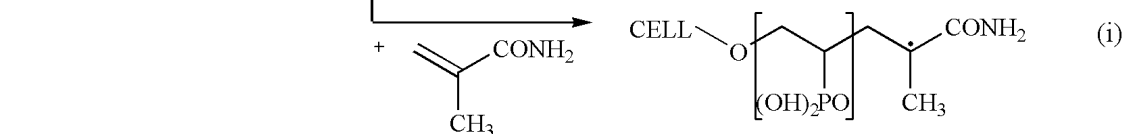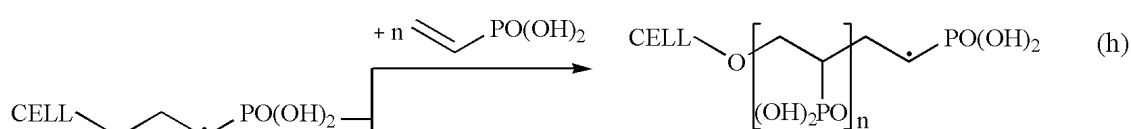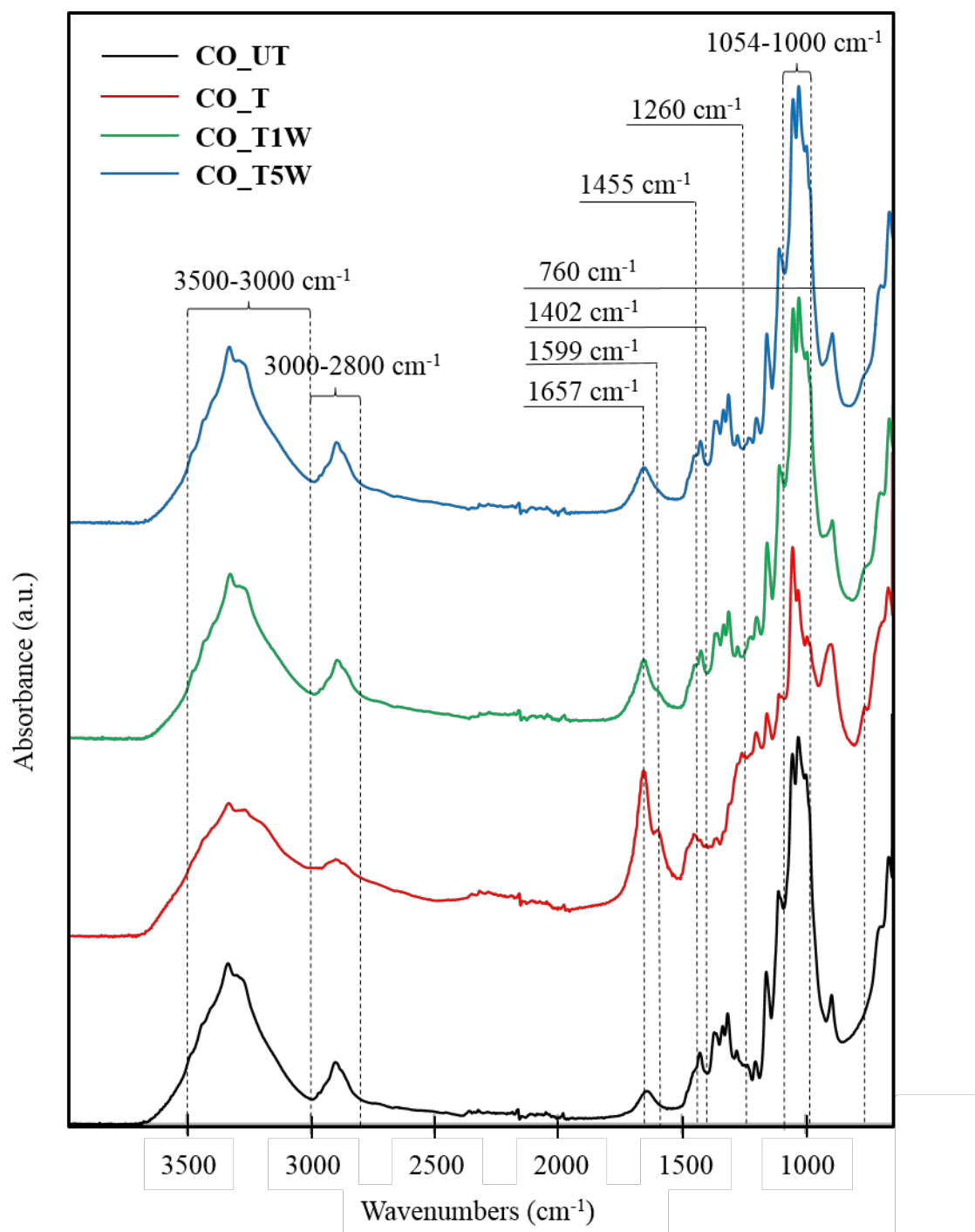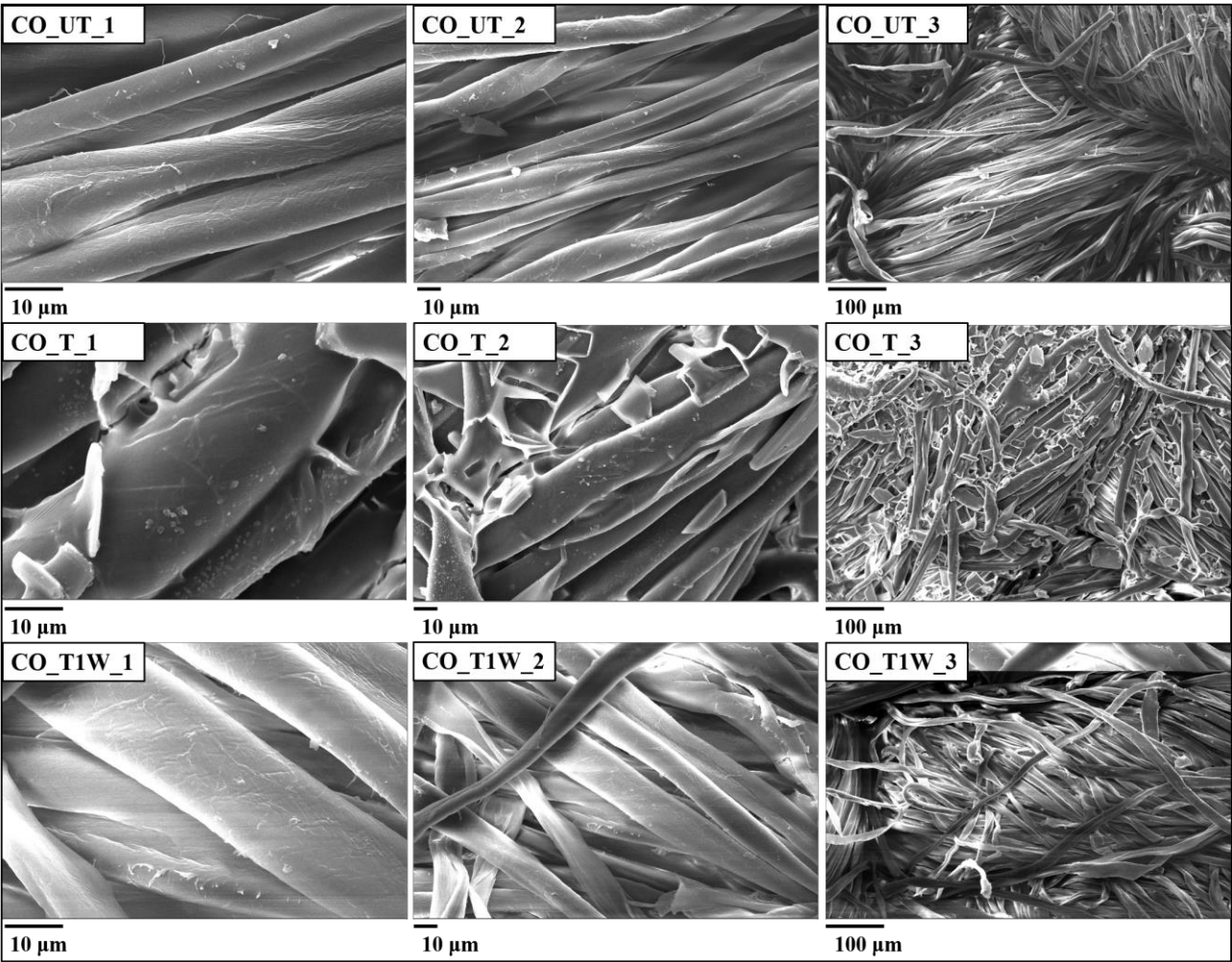
**FIGURE 1**

**FIGURE 2**

**FIGURE 3**
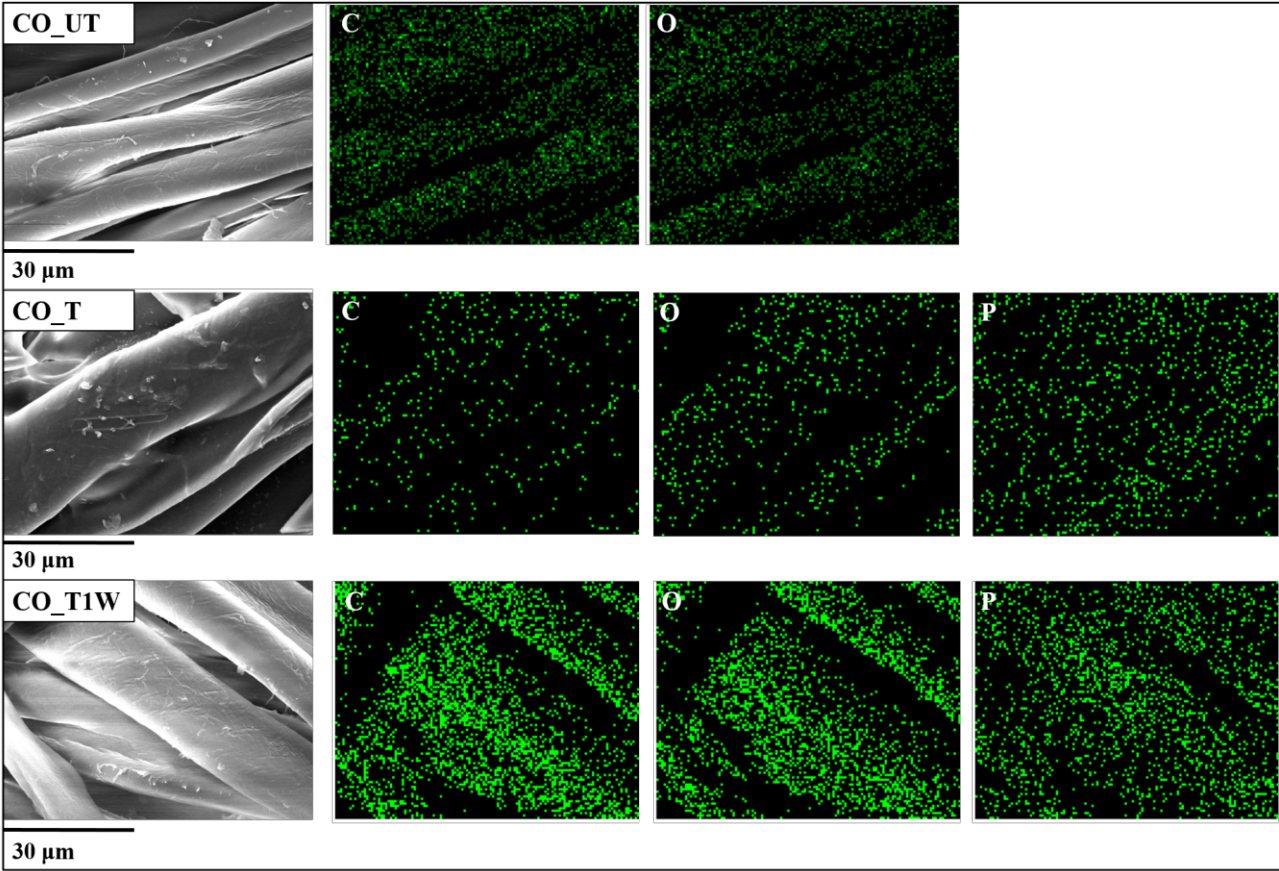
**FIGURE 4**

# FIGURE 5

**FIGURE 6**



CO_T1W@RES    C    O    P

30 μm
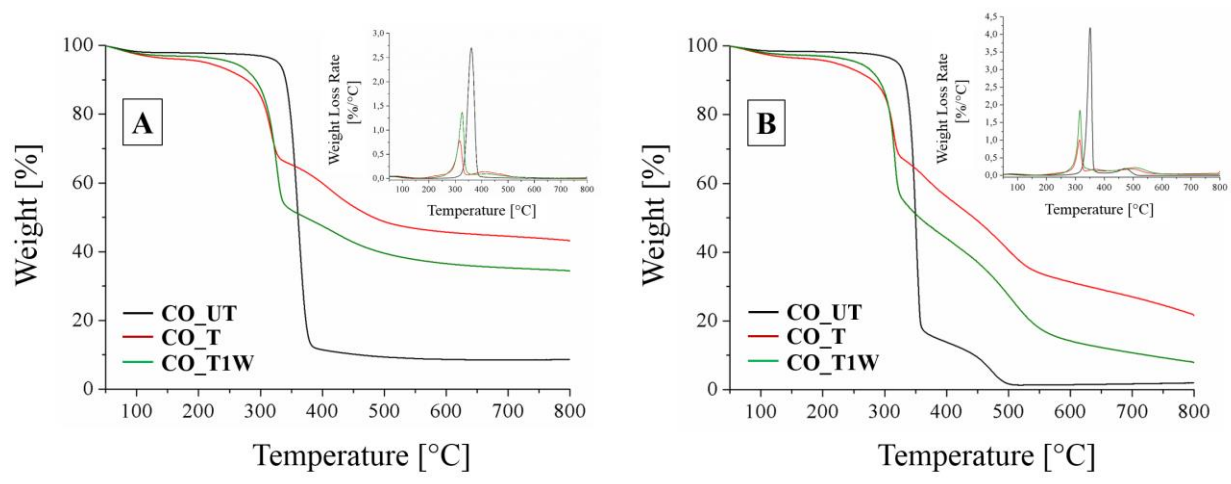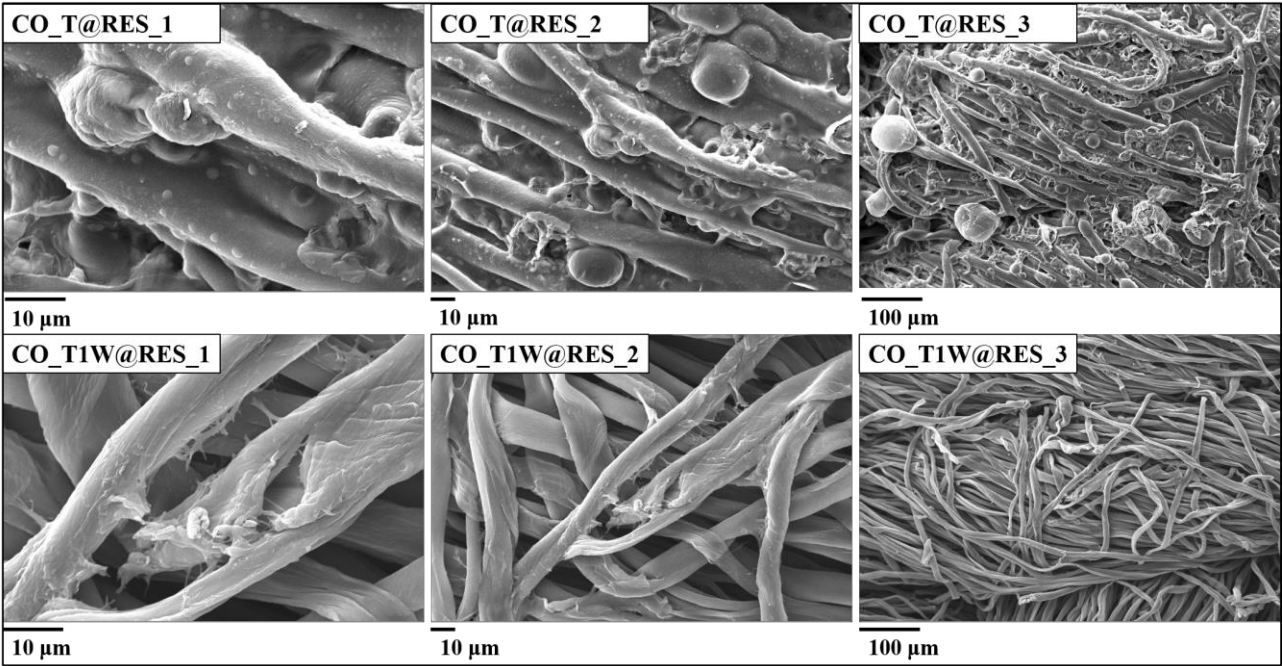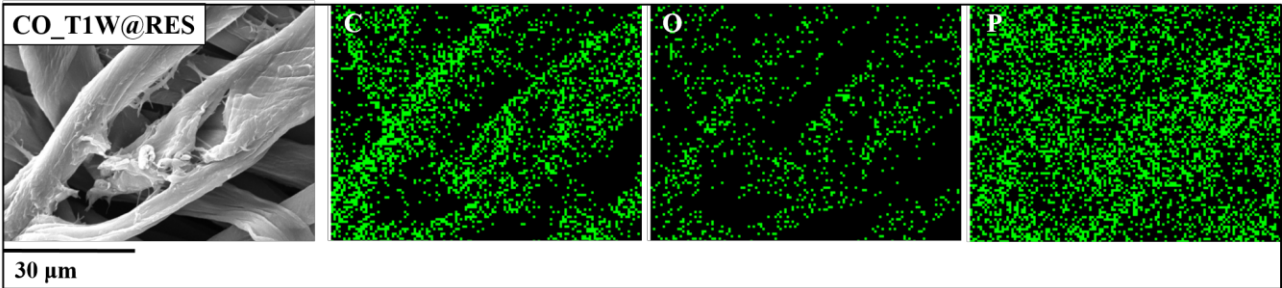
**Table 1** TG data of CO_UT, CO_T, CO_T1W in nitrogen and air atmospheres

| Sample | Atm. | $T_{onset10\%}$ (°C) | $T_{50\%}$ (°C) | $T_{max1}$ (°C) | R@ $T_{max1}$ (%) | $T_{max2}$ (°C) | R@ $T_{max2}$ (%) | $T_{max3}$ (°C) | R@ $T_{max3}$ (%) | R@ 700°C (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| CO_UT | $N_2$ | 336 | 360 | 362 | 50.3 | - | - | - | - | 8.3 |
| | Air | 330 | 349 | 351 | 41.7 | 471 | 5.6 | - | - | 1.6 |
| CO_T | $N_2$ | 253 | 468 | 317 | 72.5 | 411 | 56.7 | | | 43.4 |
| | Air | 267 | 438 | 314 | 73.2 | 369 | 60.1 | 493 | 41.0 | 26.6 |
| CO_T1W | $N_2$ | 278 | 355 | 326 | 63.2 | 419 | 44.3 | | | 34.3 |
| | Air | 284 | 352 | 315 | 67.9 | 506 | 25.7 | - | - | 10.6 |

**Table 2** Flammability behaviour and data of CO_UT, CO_T, CO_T1W and CO_T5W
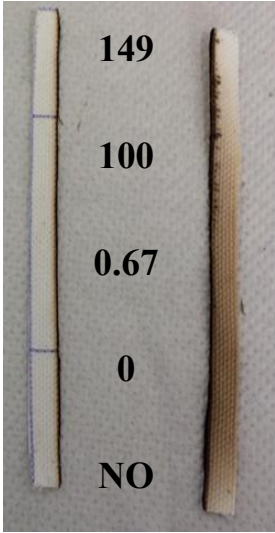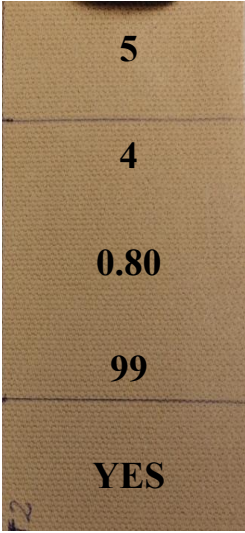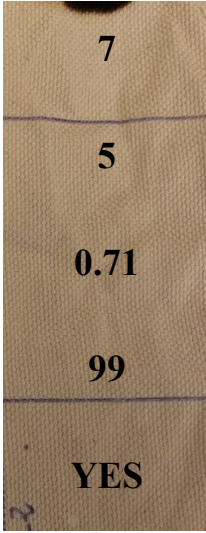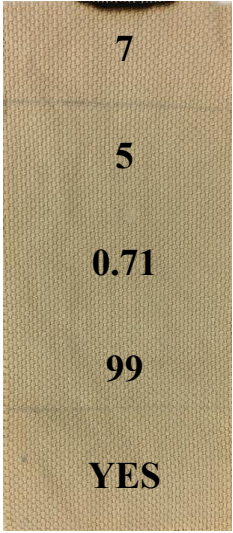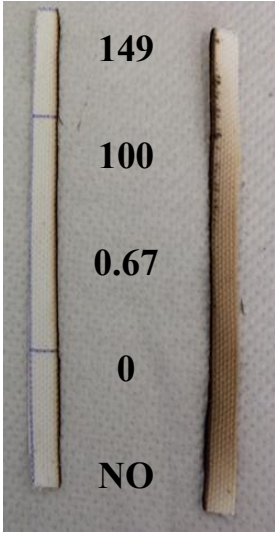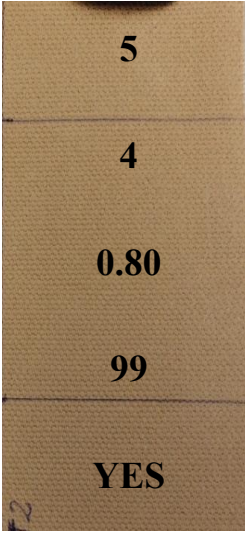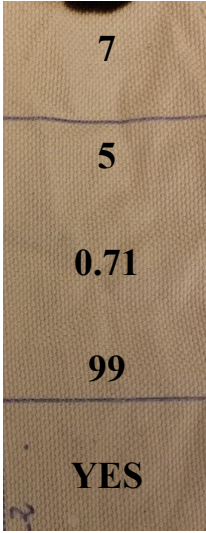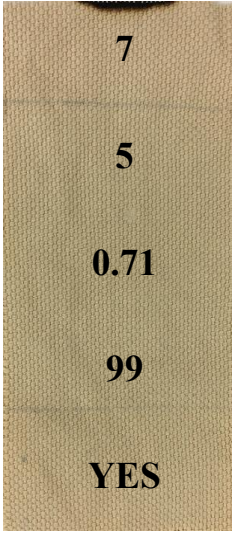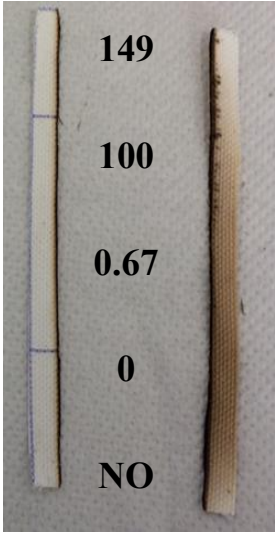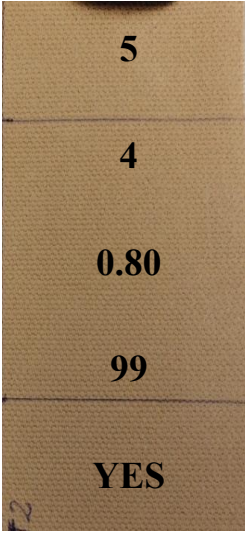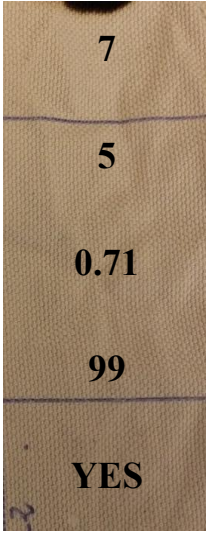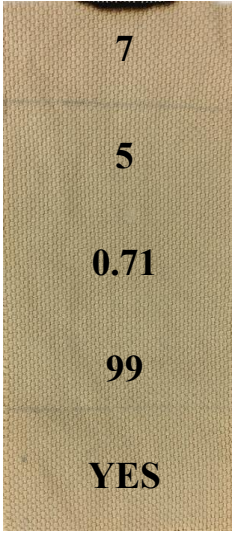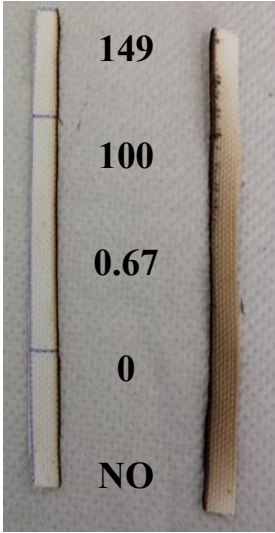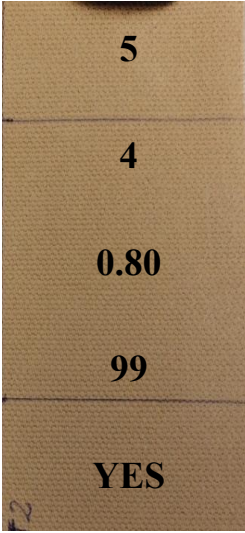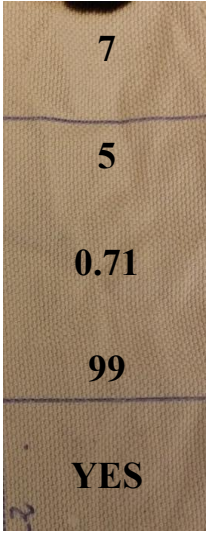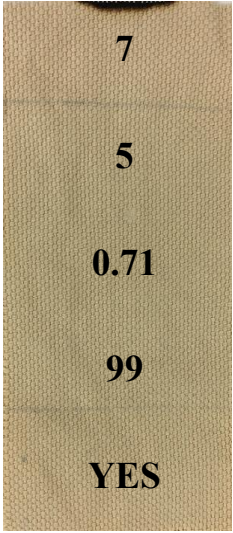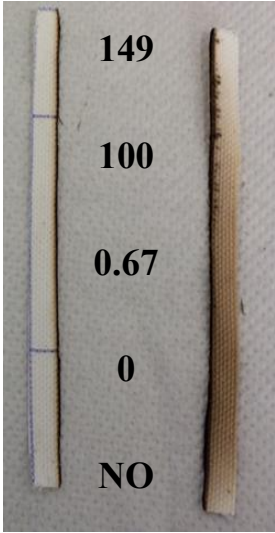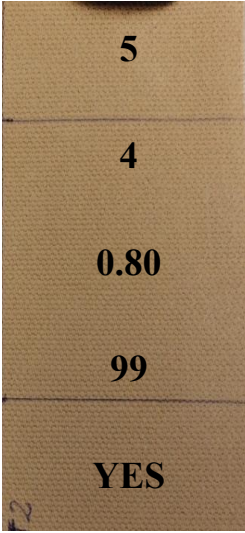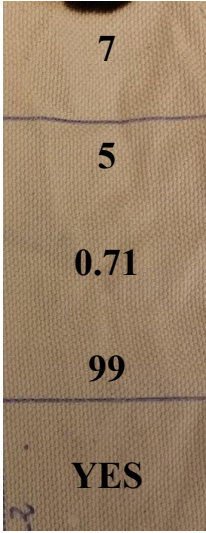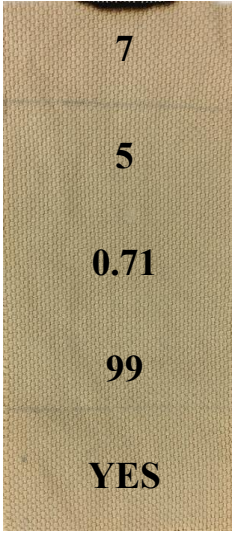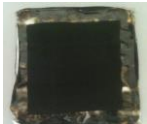
| Data | CO_UT | CO_T | CO_T1W | CO_T5W |
|---|---|---|---|---|
| Total burning time(s) | 149 | 5 | 7 | 7 |
| Char lenght (mm) | 100 | 4 | 5 | 5 |
| Total burning rate (mm/s) | 0.67 | 0.80 | 0.71 | 0.71 |
| Residue (%) | 0 | 99 | 99 | 99 |
| Self-extinction | NO | YES | YES | YES |

**Table 3** Combustion behaviour and data of CO_UT, CO_T, CO_T1W and CO_T5W from cone calorimetry tests performed at 35 kW/m$^2$

| Sample | TTI (s) | pkHRR (kW/m$^2$) | THR (MJ/m$^2$) | Residue (%) | Image |
|---|---|---|---|---|---|
| CO_UT | 26 | 175 | 5.2 | 0 |  |
| CO_T | NO IGNITION | | | 31 |  |
| CO_T1W | NO IGNITION | | | 13 |  |
| CO_T5W | NO IGNITION | | | 12 |  |