

1 **Use of calcium chloride to enhance the efficacy of polyamidoamines as flame**
2 **retardants for cotton**

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8

9 **Abstract**

10 The role of metal ions in improving the flame resistance of cotton prompted to investigate whether
11 adding CaCl₂ to the glycine-derived polyamidoamine M-GLY, an excellent intumescent flame
12 retardant for cotton, increased its efficacy in this respect. Thermogravimetric analysis
13 demonstrated a superior thermo-oxidative stability of cotton when treated with M-GLY/CaCl₂
14 mixtures, particularly above 550 °C, compared to cotton treated with either M-GLY or CaCl₂,
15 suggesting that they act synergistically. In horizontal flame spread tests, M-GLY/CaCl₂ coatings
16 proved to be even more efficient than M-GLY coatings. In vertical flame spread tests (VFSTs),
17 where M-GLY failed to protect cotton even at add-ons >30%, M-GLY/CaCl₂ coatings with add-
18 ons 7% and 2%, respectively, inhibited cotton ignition producing only modest afterglow, and
19 leaving an 82% residue. No other amino acid-derived polyamidoamine, except those containing
20 disulfide groups, has proved as efficient in VFSTs, even at much higher add-ons. The set of data
21 reported here prompts that the ionic interactions of calcium ions with the carboxylate groups of
22 M-GLY induce the formation of even larger amounts of char compared to M-GLY and lets
23 envisaging a synergistic action of these two components. This finding paves the way for the study
24 of new polyamidoamine-based organic/inorganic flame retardants for cotton.

25

26 **Keywords:** polyamidoamines; intumescent flame retardants; calcium chloride; functional
27 coatings; cotton.

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32 1. Introduction

33 Accidental fires are one of the most serious personal safety hazards worldwide. In 2020, 4.0 million
34 fires occurred in 33 countries, causing 20.7 thousand deaths [1]. About one third of them occurred
35 indoors, and another 13% involved vehicle upholstery, where fabrics, particularly cotton fabrics,
36 are often employed. It is common knowledge that cotton is one of most highly flammable textile
37 since it catches fire easily and burns quickly [2]. Understandably, several efforts have been devoted
38 to the development of effective flame retardants (FRs) for cotton. Phosphorus-based compounds,
39 such as tetrakis(hydroxymethyl) phosphonium salts (Proban®) and *N*-methyldialkyl
40 phosphonopropionamides (Pyrovatex®), have been the main FRs for cotton used over the past 40
41 years [3,4]. However, some of them have a remarkable impact on human health and environment
42 due to the proven release of formaldehyde during both manufacturing and service life [3,4].
43 Moreover, they produce fumes and smoke when activated [5]. Although new durable phosphorus-
44 based FRs have been developed [4], including triazine-based FRs, UV-curable coatings, hybrid
45 organic-inorganic FRs and polymeric additives, international regulations require more eco-
46 compatible and non-toxic cotton FRs [6].

47 Polyamidoamines (PAAs) are multifunctional polymers synthesized by the aza-Michael
48 polyaddition of *prim*- or *bis-sec*-amines, including natural α -amino acids with bis-acrylamides
49 [7,8]. They can be synthesized in water at room temperature, pH 10 and with no added catalysts.
50 Due to the type of polymerization, no by-products are formed. Many natural α -amino acid-derived
51 PAAs are biocompatible [9,10] and, as suggested by recent studies, also eco-compatible [11]. Also
52 polyamidoamines (PAAs) have recently proved to be considerably active as FRs for cotton,
53 especially so those deriving from natural amino acids [12-18]. These PAAs proved non-flammable
54 by applying a butane flame; intumescence occurred on their surface, which swelled and blackened,
55 but the interior remained unaltered [16,17]. Solid state ^{13}C nuclear magnetic resonance
56 spectroscopy (NMR) coupled with X-ray photoelectron spectroscopy (XPS) clearly indicated that
57 a glycine-derived PAA, coded M-GLY, promoted carbonization of cotton with formation of highly
58 condensed aromatic structures, suggesting the existence of a nanographitic char [17]. Deposited
59 on cotton, these PAAs extinguished the flame in horizontal flame spread tests (HFSTs) at add-ons
60 as low as 4-7% [12], whereas most PAAs, including M-GLY, failed in vertical flame spread tests
61 (VFSTs), with the only exception of the cystine-based polymers and glycine/cystine copolymers
62 [15]. In all cases, the burnt cotton areas retained the original texture and showed intumescent

63 microbubbles [12,17], as revealed by scanning electron microscopy (SEM). In oxygen
64 consumption cone calorimetry tests, amino acid-derived PAAs increased the resistance of cotton
65 to a 35 kWm^{-2} irradiative heat flux, which is normally found in developing fires. They also reduced
66 the heat release rate peak and the production of carbon oxides, leaving over 80% intact residual
67 mass fraction. No smoke release was observed in these tests. Thermogravimetric analyses (TGA)
68 showed that amino acid-derived PAAs sensitized cotton to thermal decomposition and intumesced
69 when heated in air at $350 - 450 \text{ }^\circ\text{C}$, the temperature range where cotton undergoes thermo-
70 oxidation.

71 It has been widely demonstrated that inorganic salts influence the thermal decomposition pathway
72 of cellulose [19-29]. They generally reduce both the onset decomposition temperature and the
73 maximum weight loss temperature and influence the distribution of the decomposition products.
74 In their presence, cellulose preferentially undergoes dehydration rather than depolymerization
75 [24,25] generating thermally stable aromatic chars [26-28]. The effect of inorganic salts has been
76 ascribed to their ionic nature and their Lewis acidity or basicity strength on which the ability to
77 stabilize specific reaction intermediates depends [19]. Furthermore, studies carried out with water
78 insoluble Zn- and Co-ethylhexanoates demonstrated that also these organic salts increased char
79 formation at $600 \text{ }^\circ\text{C}$ [22]. The presence of ethylhexanoic acid in the pyrolyzed gases suggested the
80 occurrence of an exchange reaction between the metal ions and the hydrogens of the cellulose
81 hydroxyl groups. Concerning the effect of Ca^{2+} , it has been reported that increasing amounts of
82 CaCl_2 shifted progressively the entire thermal decomposition pattern earlier and led to increasing
83 char residues at $800 \text{ }^\circ\text{C}$ [23]. In fact, in a previous paper, it had been hypothesized that Ca^{2+} interact
84 with the hydroxyl groups of the glycosidic monomeric unit of cellulose, therefore promoting
85 dehydration and fragmentation, which represent a prelude to char formation, instead of producing
86 levoglucosan and other depolymerization fragments [21]. Fast pyrolysis tests of cellulose in the
87 presence of MgCl_2 and NaCl confirmed that both salts enhanced the ring opening of the pyranose
88 residues above $250 \text{ }^\circ\text{C}$ [29].

89 Metal ions have also been shown to influence the thermal oxidative behavior of cotton fabrics
90 coated with bio-based layer-by-layer assemblies [30]. Furthermore, it was also shown that metal
91 ions with Lewis acid characteristics [31-34], not only sensitized char formation in pure cellulose
92 in air, but also promoted the thermal degradation of ammonium polyphosphate, used as
93 intumescent flame retardant for cotton, thus favoring the flame resistance of cotton.

94 Based on this premise, it was thought it will be interesting to ascertain whether Ca^{2+} could
95 influence the thermal-oxidative stability of amino acid-derived PAAs and of PAA-impregnated
96 cotton by establishing ionic interactions with the carboxylate pendants or Lewis acid/base
97 interactions with the amide $\text{C}=\text{O}$ present in the repeat units of these PAAs and, furthermore, if
98 these interactions could improve the PAA flame retardant activity. To this aim, in this work we
99 have investigated in detail the performance of CaCl_2 -based formulations of the glycine-derived
100 PAA named M-GLY, which failed to quench combustion in vertical flame spread tests, which are
101 the most realistic fire tests for textiles, even at add-on higher than 30%.

102

103 **2. Experimental part**

104 *2.1 Materials*

105 Glycine (GLY, >98%), *N,N'*-methylenebisacrylamide (M, 99%), lithium hydroxide monohydrate
106 ($\text{LiOH}\cdot\text{H}_2\text{O}$, 98%), calcium chloride (CaCl_2 , >97%), hydrochloric acid (HCl, 37% w/w aqueous
107 solution) and deuterium oxide (D_2O , 99.9%) were purchased from Sigma-Aldrich (Milano, Italy)
108 and used as received. Aqueous solutions were prepared using deionized water obtained with a Q20
109 Millipore system. Cotton fabric (COT) having an area density of 200 gm^{-2} was purchased from
110 Fratelli Ballesio S.r.l. (Torino, Italy).

111

112 *2.2 Characterization techniques*

113 The thermal and thermal oxidative stability of M-GLY, M-GLY-, Ca^{2+} - and M-GLY- Ca^{2+} -treated
114 cotton fabrics were evaluated by thermogravimetric analysis (TGA) from 50 to $800 \text{ }^\circ\text{C}$ with
115 heating rate $10 \text{ }^\circ\text{C min}^{-1}$. A Perkin Elmer thermogravimetric balance, TGA 7 - Thermogravimetric
116 Analyzer, was used, placing samples (5 mg) in open platinum pans, in either nitrogen or air under
117 20 mL min^{-1} gas flow (Perkin Elmer, Milano, Italy). The surface morphologies of untreated and
118 PAA-treated cotton, and combustion residues were characterized using an EVO 15 equipped with
119 a ULTIM MAX 40 probe scanning electron microscope (SEM) (Zeiss, Ramsey, NJ, USA),
120 operating at 8.5 mm working distance, under 5 kV beam voltage, equipped with Energy-Dispersive
121 X-ray Spectroscopy (EDX, Jena, Germany) to perform elemental analyses. Small square samples
122 of unburnt or burnt fabrics (5 mm x 5 mm) were fixed to the sample holder through conductive
123 adhesive tapes and then gold metalized.

124

125 *2.3 Synthesis of glycine-derived polyamidoamine*

126 M-GLY was synthesized as already reported [12]. Briefly, *N,N'*-methylenebisacrylamide (M, 4.11
127 g; 0.03 mol), glycine (GLY, 2.00 g; 0.03 mol), and lithium hydroxide monohydrate (LiOH·H₂O,
128 1.14 g; 0.03 mol) were suspended in water (9 mL). The reaction mixture was then heated to 50-55
129 °C until complete dissolution of M and left for 5 days at 25 °C in the dark. After this time, the
130 reaction mixture was diluted to 25 mL with water, the pH adjusted to 4.5 with 37% hydrochloric
131 acid and the acidified solution freeze-dried to retrieve the solid product. The yield approached
132 100%.

133

134 *2.4 Impregnation of cotton fabrics*

135 Strips of cotton fabrics with 40 mm x 80 mm size were dried for 4 min at 110 °C then maintained
136 at room temperature for 10 min and then weighed. After this time, the weight was usually constant.
137 Subsequently, the cotton samples were impregnated twice with 2 mL of an aqueous solution of the
138 M-GLY at a concentration useful to obtain the desired add-on (see below), by adding 10 aliquots
139 of 200 µl each. The impregnated samples were dried for 4 min at 110 °C, kept at room temperature
140 for 10 min and then weighed. The total dry solid add-ons (*Add-on*, wt.%) were determined by
141 means of Eq. (1)

142

$$143 \quad \text{Add-on} = \frac{W_f - W_i}{W_i} \times 100 \quad (1)$$

144

145 where W_i is the weight of the dry cotton sample before impregnation and W_f the weight of the dry
146 cotton sample after impregnation. The concentrations of the impregnating M-GLY solutions were:
147 3.5 wt.% for 7% add-on (used in horizontal flame spread tests) and 9.5 wt.% for 19% add-on (used
148 in vertical flame spread tests). The add-on adopted in vertical flame spread tests were superior to
149 those adopted in horizontal flame spread tests, since the vertical configuration represents a more
150 severe fire scenario, being the combustion forced by the chimney effect.

151 CaCl₂ add-on was maintained at 2%. This add-on value was obtained by adding once 2 mL of a 2
152 wt.% of aqueous CaCl₂ solution, regardless of the presence of M-GLY.

153 Treated cotton fabrics were coded either COT/M-GLY or COT/Ca²⁺ or COT/M-GLY-
154 Ca²⁺ depending on whether they were treated either with M-GLY, or CaCl₂, or M-GLY plus CaCl₂,
155 respectively.

156 2.5 Combustion tests

157 The ignitability of M-GLY (350 mg) and of a M-GLY/CaCl₂ mixture (350 mg of M-GLY and 25
158 mg of CaCl₂) was assessed by applying a butane flame of 20 mm length for 20 s to the powdered
159 sample placed on a porcelain surface. The M-GLY/CaCl₂ mixture was obtained by grinding
160 together the two components in a pestle and mortar to ensure homogenous dispersion. Before
161 testing, the specimens were conditioned at 27 ± 1 °C and 50% relative humidity in a climate
162 chamber until constant weight. All experiments were performed in duplicate.

163 Combustion flame spread tests were carried out placing rectangular cotton strips (40 mm x 80 mm)
164 in a metallic frame placed in horizontal or vertical configuration according to the ISO 3795 [35]
165 and ISO 15025 [36] standards modified in terms of cotton size specimens and flame application
166 time. In horizontal flame spread tests (HFSTs), the shorter side of the specimen was tilted by 45°
167 with respect to the vertical axis. In both configurations, the cotton specimens were impinged on
168 the shorter side by a butane flame of 20 mm length. The flame contact time was 3 s in HFSTs and
169 2 s in vertical flame spread tests (VFSTs). All tests were repeated in sextuplicate. Flaming
170 combustion time (s), afterglow combustion time (s) and residual mass fraction (RMF, wt.-%) were
171 assessed and compared with those of untreated cotton.

172 The resistance to a 35 kWm⁻² irradiative heat flux of square fabric samples (100 mm x 100 mm)
173 was investigated using an oxygen-consumption cone calorimeter (Noselab Ats Srl, Bovisio-
174 masciago, Monza-Brianza, Italy). Measurements were carried out in horizontal configuration,
175 following a procedure previously reported [37] based on the ISO 5660 standard [38]. Parameters
176 such as time to ignition (TTI, s), heat release rate peak (pkHRR, kWm⁻²), total heat release (THR,
177 MJm⁻²) and residual mass fraction (RMF, wt.-%) were determined. Prior to the combustion tests,
178 all specimens were conditioned to constant weight at 23 ± 1 °C for 48 h at 50% relative humidity
179 in a climatic chamber. Each experiment was performed in triplicate and the standard deviation
180 calculated.

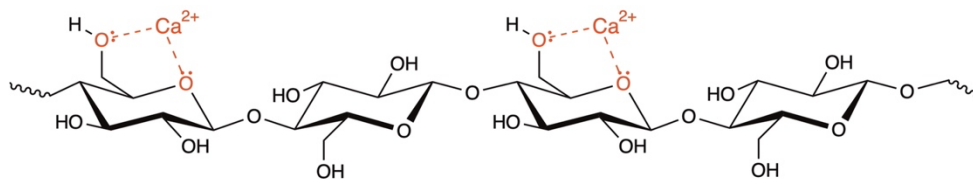
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182 3. Results and discussion

183 3.1 Rationale

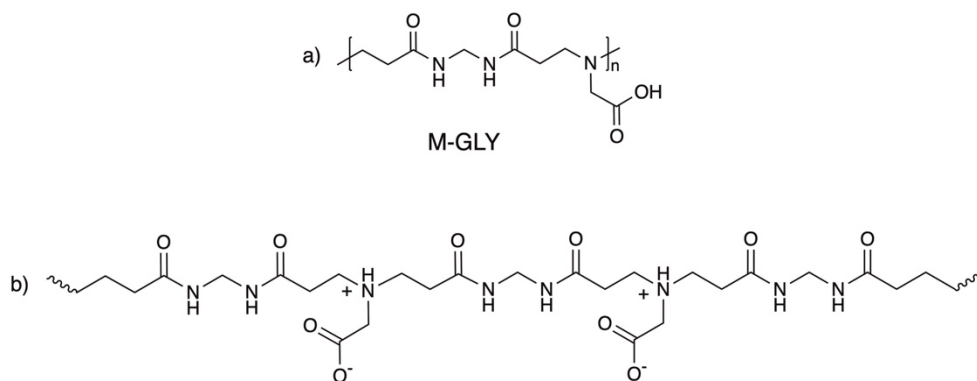
184 In previous articles it has been hypothesized that Ca²⁺ ions, which are good Lewis acids [39],
185 can interact with both the ether and the hydroxyl groups of cellulose pyranose ring (Fig. 1),
186 promoting the homolytic cleavage of the covalent bonds of the pyranose ring [19]. This thermal

187 decomposition pattern explains the formation of low molecular weight decomposition products
 188 including, among others, glycolaldehyde, acetol, and formic, and compete with the heterocyclic
 189 cleavage of the glycosidic linkages resulting in depolymerization and release of levoglucosan.

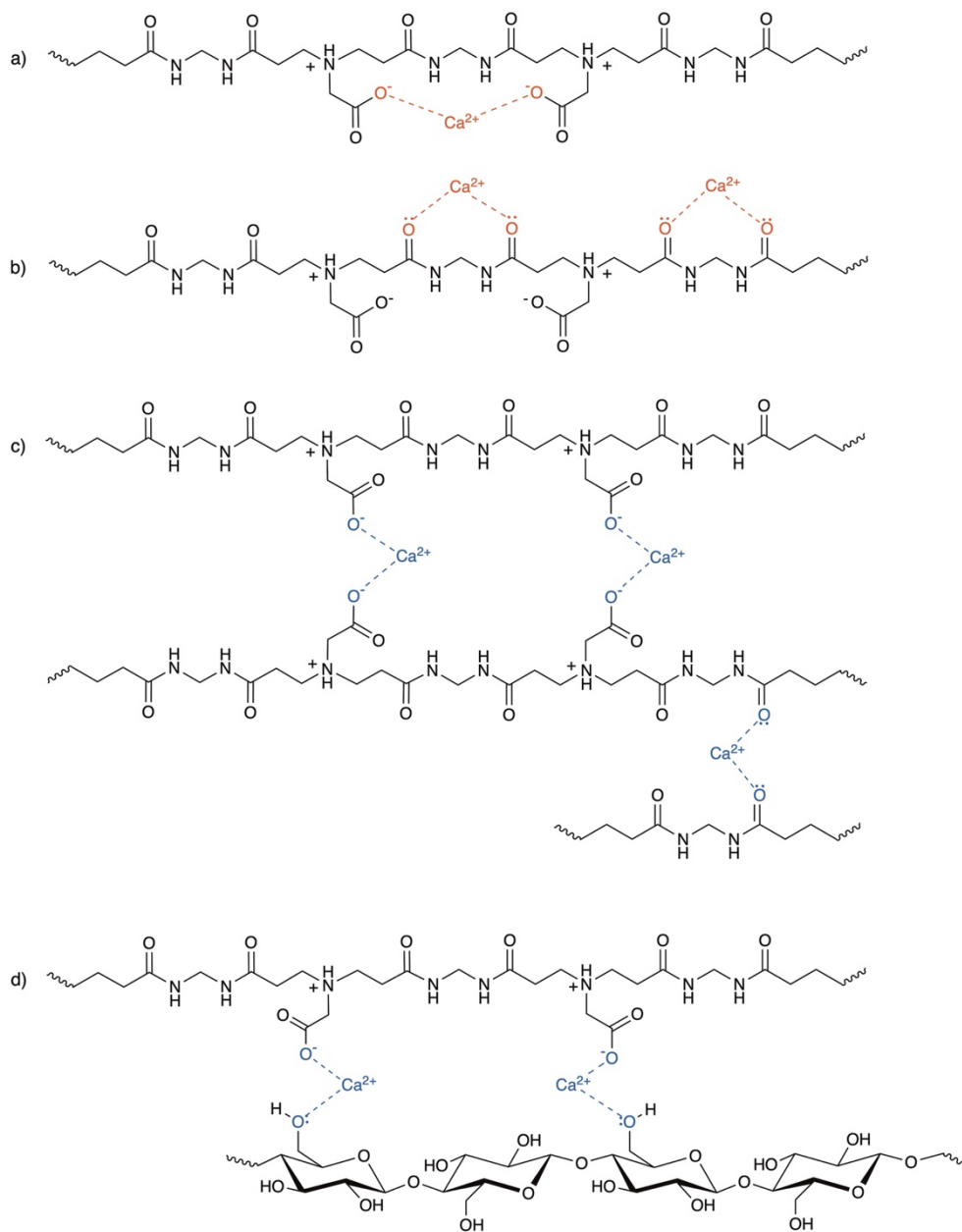


190
 191 **Fig. 1.** Interaction of cellulose with Ca^{2+} ions [19].
 192

193 The glycine-derived PAA coded M-GLY (Fig. 2a), bearing in its repeat unit a *tert*-amine group
 194 and a carboxyl pendant, is a water-soluble amphoteric polymer with isoelectric point 4.8. At pH
 195 5.0, at which the M-GLY is deposited onto cotton, its repeat units bear approximately 100%
 196 protonated *tert*-amine groups in the backbone (*tert*-amine $pK_a = 7.7$) and 100% carboxylate
 197 pendants ($\text{COOH } pK_a = 1.9$) (Fig. 2b). The relative amount of these two ionizable groups
 198 obviously change with pH, although the carboxyl pendants are always present in the deprotonated
 199 form in a wide pH range. Due to the presence of lithium carboxylate (Scheme 1) and secondary
 200 amide groups in all M-GLY repeat units, Ca^{2+} ions can give rise to intra- or inter-molecular ionic
 201 exchange reactions, as well as Lewis acid/base interactions with the amide $\text{C}=\text{O}$ groups (Fig. 3a-
 202 c). Furthermore, Ca^{2+} ions can act as a bridge between M-GLY and cellulose by exploiting
 203 different ionic and Lewis acid/base interactions (Fig. 3d). The aim of this work is to investigate
 204 the effect of this set of interactions on the thermal oxidative stability of cotton fabrics coated with
 205 both M-GLY and CaCl_2 and, particularly, if these may give rise to synergistic actions.



206 **Fig. 2.** M-GLY repeat unit: structure (a) and pH-dependent ionic species distribution (b).
 207

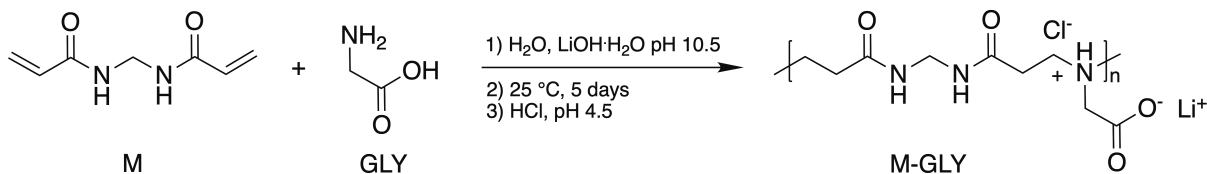


208

209 **Fig. 3.** Examples of possible intramolecular and intermolecular ionic and Lewis acid/base interactions of Ca^{2+} ions
 210 with the repeat units of M-GLY and cellulose: intramolecular M-GLY/ Ca^{2+} interactions (in red **a,b**); intermolecular
 211 M-GLY/ Ca^{2+} interactions (in blue **c**); intermolecular M-GLY/ Ca^{2+} /cellulose interactions (in blue **d**).

212 3.2 Synthesis of the glycine-derived polyamidoamine M-GLY and its interaction with Ca^{2+} ions

213 M-GLY was synthesized by the aza-Michael polyaddition of *N,N'*-methylenebisacrylamide (M)
 214 with glycine (GLY) (Scheme 1), following an already reported procedure [12]. The M-GLY
 215 structure was confirmed by $^1\text{H-NMR}$ and FT-IR/ATR spectroscopies (Fig. S1 and S2 in
 216 Supporting Information, respectively).



Scheme 1. Synthesis of M-GLY.

217
218
219

220 The interaction mode of the Ca^{2+} ions with the M-GLY was investigated by means of FT-IR (Fig.
221 S2a). The spectrum of the M-GLY- Ca^{2+} system, compared with those of M-GLY and CaCl_2 ,
222 showed significant changes with respect to those of M-GLY and CaCl_2 alone in well-defined
223 spectral ranges. In particular, the IR spectrum of M-GLY exhibited two diagnostic peaks placed at
224 1626 and 1529 cm^{-1} . The first is due to the overlapping of the carboxylate stretching band and the
225 so-called amide I band, the second to the amide II band. It is apparent that in the M-GLY- Ca^{2+}
226 system the amide II band, that is, the amide N-H bending, reduced and broadened significantly,
227 whereas a new narrow band appeared at 1613 cm^{-1} (Fig. S2b). This change can be attributed to the
228 interaction of the Ca^{2+} ions with the amide $\text{C}=\text{O}$ groups, which alters the strength of the hydrogen
229 bond involving the amide N-H and causes a shift to higher wavenumbers. This peculiar effect of
230 the Ca^{2+} interaction with the amide groups of polymers has been already reported, inter alia, in the
231 case of PA6,6 [40]. Not unexpectedly, the carboxylate stretching band did not apparently shift
232 following the lithium/calcium ion exchange. A second relevant change involving the vibrational
233 mode of the N-H group was observed in the $3000\text{-}3500 \text{ cm}^{-1}$ spectral region, where M-GLY
234 exhibited a broad band due to the amide N-H stretching, which converted into a narrow bimodal
235 band centered at 3442 and 3493 cm^{-1} . It can be finally observed that the Ca-Cl band placed in pure
236 CaCl_2 at 649 cm^{-1} [41] disappeared in the spectrum of the spectrum of the M-GLY- Ca^{2+} system.
237

238 3.3 Thermal stability of M-GLY- Ca^{2+} and M-GLY

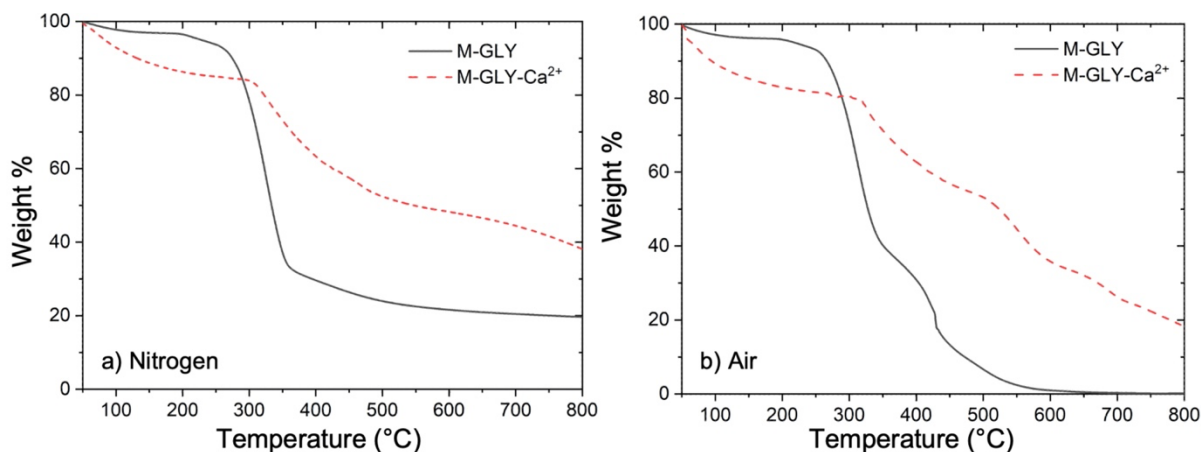
239 Fig. 4 shows the TG thermograms between 50 and $800 \text{ }^\circ\text{C}$ both in nitrogen and in air of a 3.5:1
240 (w/w) homogeneous M-GLY/ CaCl_2 mixture, coded as M-GLY- Ca^{2+} , and M-GLY. The selected
241 M-GLY/ CaCl_2 weight ratio is the same as the mixture applied on cotton fabrics in horizontal flame
242 spread tests (section 2.4). The relevant thermal data are collected in Table 1. To ensure the most
243 even distribution of the two components, the M-GLY- Ca^{2+} mixture was prepared by dissolving in
244 water M-GLY and CaCl_2 in suitable amounts and then freeze-drying the resultant mixed solution.
245 It should be observed that in Fig. 4 the thermogram of CaCl_2 is not shown, since it is known that

246 in anhydrous conditions CaCl_2 dehydrates in between 180 - 260 °C, and then is stable up to around
247 800 °C [40].

248 Consistent with previous findings [12], in nitrogen M-GLY mainly decomposed in between 250-
249 350 °C with an overall weight loss of about 65% (Fig. 4a). The residue formed at 350 °C slowly
250 decomposed at higher temperatures, until leaving a residual mass fraction at 800 °C, RMF_{800} , of
251 20.0% (Table 1). In M-GLY- Ca^{2+} , the presence of Ca^{2+} induced M-GLY dehydration at a lower
252 $T_{\text{onset}10\%}$ (Fig. 4a, Table 1), while shifting the onset of thermal decomposition to 300 °C, *i.e.*, by 50
253 °C higher than for M-GLY alone. The residue formed at 300 °C underwent further slow
254 decomposition between 300 and 800 °C, an interval within which two maximum weight loss
255 temperatures were identified, namely $T_{\text{max}1} = 344$ °C and $T_{\text{max}2} = 550$ °C. Additionally, M-GLY-
256 Ca^{2+} left a significantly higher RMF_{800} compared to M-GLY (37.0% including a 2% CaCl_2 residue
257 *vs.* 20.0%).

258 In air, both M-GLY- Ca^{2+} and M-GLY showed multimodal weight loss curves (Fig. 4b). In detail,
259 M-GLY decomposed through a two-step pathway, with a first weight loss from 250 to 350 °C of
260 about 50%, *i.e.*, significantly lower than in nitrogen. Overall, the TG trace of M-GLY in air showed
261 a significantly lower weight loss in the whole 300-570 °C temperature range than in nitrogen, due
262 to the well-known intumescent behavior of this polymer, which generated in air an expanded
263 carbonaceous char [12,17]. This char further oxidized at higher temperatures until leaving an
264 almost negligible RMF_{800} (Table 1). In air, M-GLY- Ca^{2+} was significantly more stable than in
265 nitrogen and much more stable than M-GLY in air. In the latter environment, three main weight
266 phenomena were observed in the 320-800 °C range: a first weight loss of only about 30% in
267 between 320-450 °C, a second weight loss of 30% in the 450-550 °C range, and a slow oxidation
268 from 550 °C upward until an RMF_{800} of about 19%, including a 2% CaCl_2 residue (Table 1). Such
269 a high thermal stability in air over a wide temperature range (from 300 to 800 °C), associated with
270 a residual mass fraction at 800 °C of 19% have never been observed in PAAs and represent an
271 exceptional result. The set of data collected suggests that CaCl_2 has a stabilizing effect on M-GLY.
272 This might be ascribed to the establishment of intermolecular and/or intramolecular interactions,
273 either ionic or Lewis acid/base interactions, between Ca^{2+} ions and the functional groups present
274 in the M-GLY repeat units (Fig. 3a-c).

275



276
277 **Fig. 4.** TG thermograms of M-GLY-Ca²⁺ and M-GLY in nitrogen (a) and in air (b). The 3.5:1 M-GLY/CaCl₂ ratio
278 (w/w) in M-GLY-Ca²⁺ is the same used in HFSTs.

279
280 **Table 1**

281 Thermal data of M-GLY-Ca²⁺ and M-GLY in nitrogen and in air by thermogravimetric analysis.

Sample	T _{onset10%} ^{a)} (°C)	T _{max1} ^{b)} (°C)	T _{max2} ^{c)} (°C)	RMF ₈₀₀ ^{d)} (%)
<i>Nitrogen</i>				
M-GLY	277	325	-	20.0
M-GLY-Ca ²⁺ ^{e)}	127	344	550	37.0 ^{f)}
<i>Air</i>				
M-GLY	267	310	428	0
M-GLY-Ca ²⁺ ^{e)}	162	320	430	19.0 ^{f)}

282 ^{a)} Onset decomposition temperature at 10% weight loss. ^{b)} First temperature at maximum weight loss rate obtained
283 from the derivative thermogravimetric curve of Fig. S4a and Fig. S4b. ^{c)} Second temperature at maximum weight loss
284 rate obtained from the derivative thermogravimetric curve of Fig. S4a and Fig. S4b. ^{d)} Residual mass fraction at 800
285 °C. ^{e)} 3.5:1 M-GLY/CaCl₂ ratio (w/w). ^{f)} this value includes a 2% CaCl₂ residue.

286 287 3.4 Ignitability of M-GLY-Ca²⁺ and M-GLY

288 The ignitability of M-GLY-Ca²⁺ and M-GLY was assessed by direct flame impingement for 10 s
289 on neat powders (Fig. 5). The results obtained showed that there is no significant difference in char
290 formation and expansion of M-GLY in the presence of CaCl₂ compared to M-GLY alone [12]. A
291 comparable weight loss, namely 99% and 98% for M-GLY-Ca²⁺ and M-GLY, respectively, was
292 indeed found.

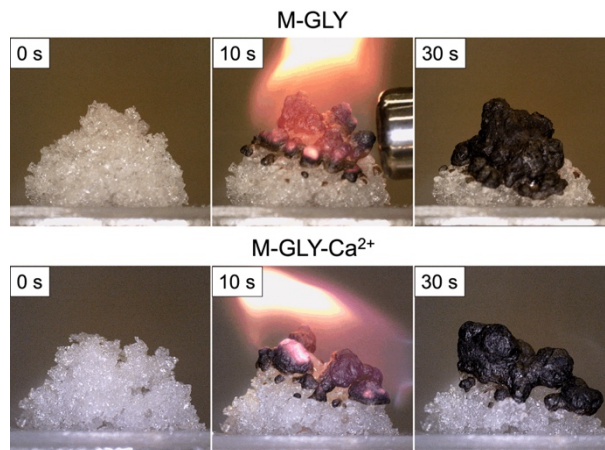


Fig. 5. Snapshots of the ignitability tests of M-GLY and M-GLY-Ca²⁺.

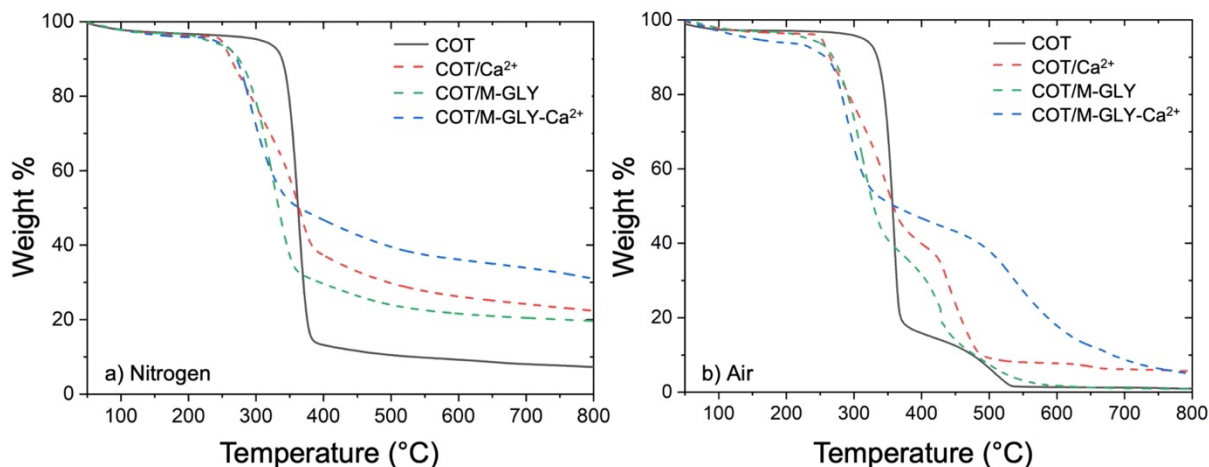
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3.5 Thermal stability of M-GLY-Ca²⁺- and M-GLY-treated cotton fabrics

297 The TG thermograms of M-GLY-Ca²⁺-treated cotton with 7% M-GLY add-on and 2% CaCl₂ add-
298 on obtained from 50 to 800 °C in nitrogen and in air were compared with those of cotton treated
299 with either M-GLY (add-on 7%) or CaCl₂ (add-on 2%), and with those of untreated cotton (Fig.
300 6). The relevant thermal data are collected in Table 2. Overall, CaCl₂, M-GLY and M-GLY-Ca²⁺
301 sensitized the thermal decomposition of cotton by reducing the T_{onset10%} values in both
302 atmospheres, while significantly increasing the residue formation at T >400 °C, although with
303 qualifications [34]. In nitrogen, after the first weight loss, untreated cotton left an RMF of about
304 10%, at around 380 °C, while M-GLY- and Ca²⁺-treated cotton left an RMF of about 30% and
305 38%, respectively, at around 350 °C. Noticeably, M-GLY-Ca²⁺-treated cotton left an RMF of about
306 55% at 350 °C (including a 2% CaCl₂ residue), *i.e.*, by far higher than those left by cotton treated
307 with M-GLY and CaCl₂ alone (Fig. 6a). Above 350 °C, the chars further decomposed leaving in
308 all cases particularly high RMF₈₀₀ values, specifically for COT/M-GLY-Ca²⁺ (31.0%, including a
309 2% CaCl₂ residue, Table 2).

310 In air, the thermal stability of the coated cotton samples was much higher than that of untreated
311 cotton, particularly in the range 350-450 °C for COT/Ca²⁺ and COT/M-GLY, within which PAAs
312 normally undergo significant intumescence [17], and in the range 350-650 °C for COT/M-GLY-
313 Ca²⁺ (Fig. 6b). Additionally, the fact that above 550 °C the residual mass values of COT/M-GLY-
314 Ca²⁺ (30% including 2% CaCl₂ residue) are much higher than the sum of those of COT/Ca²⁺ and
315 COT/M-GLY (8% and 1%, respectively) is a clear indication that M-GLY and CaCl₂ act
316 synergically as thermally protective coating of cotton. This is most likely due to the intramolecular

317 and/or intermolecular ionic and Lewis acid/base interactions between M-GLY and Ca²⁺ (Fig. 3a-
 318 c) and/or to the concomitant presence of intermolecular M-GLY/Ca²⁺/cellulose interactions (Fig.
 319 3d).
 320



321
 322
 323 **Fig. 6.** TG thermograms of untreated cotton (COT), and Ca²⁺-, M-GLY-, M-GLY-Ca²⁺-treated cotton fabrics in
 324 nitrogen (a) and air (b). COT/M-GLY add-on: 7%; COT/Ca²⁺ add-on: 2%; COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂
 325 and 7%, M-GLY.
 326

327 **Table 2**

328 Thermal data of M-GLY-Ca²⁺- and M-GLY-treated cotton fabrics in nitrogen and air by
 329 thermogravimetric analysis.

Sample	T _{onset10%} ^{a)} (°C)	T _{max1} ^{b)} (°C)	T _{max2} ^{c)} (°C)	RMF ₈₀₀ ^{d)} (%)
<i>Nitrogen</i>				
COT	342	364	-	7.5
COT/M-GLY ^{e)}	270	325	-	20.0
COT/Ca ²⁺ ^{f)}	270	270/360	-	20.5
COT/M-GLY-Ca ²⁺ ^{g)}	267	285	-	31.0 ^{h)}
<i>Air</i>				
COT	335	361	450	<1.0
COT/M-GLY ^{e)}	270	316	427	1.0
COT/Ca ²⁺ ^{f)}	270	350	440/468/649	5.5
COT/M-GLY-Ca ²⁺ ^{g)}	264	286	538	5.5 ^{h)}

330 ^{a)} Onset decomposition temperature at 10% weight loss. ^{b)} First temperature at maximum weight loss rate obtained
 331 from the derivative thermogravimetric curve of Fig. S4c and Fig. S4d. ^{c)} Second temperature at maximum weight loss
 332 rate obtained from the derivative thermogravimetric curve of Fig. S3c and Fig. S3d. ^{d)} Residual mass fraction at 800

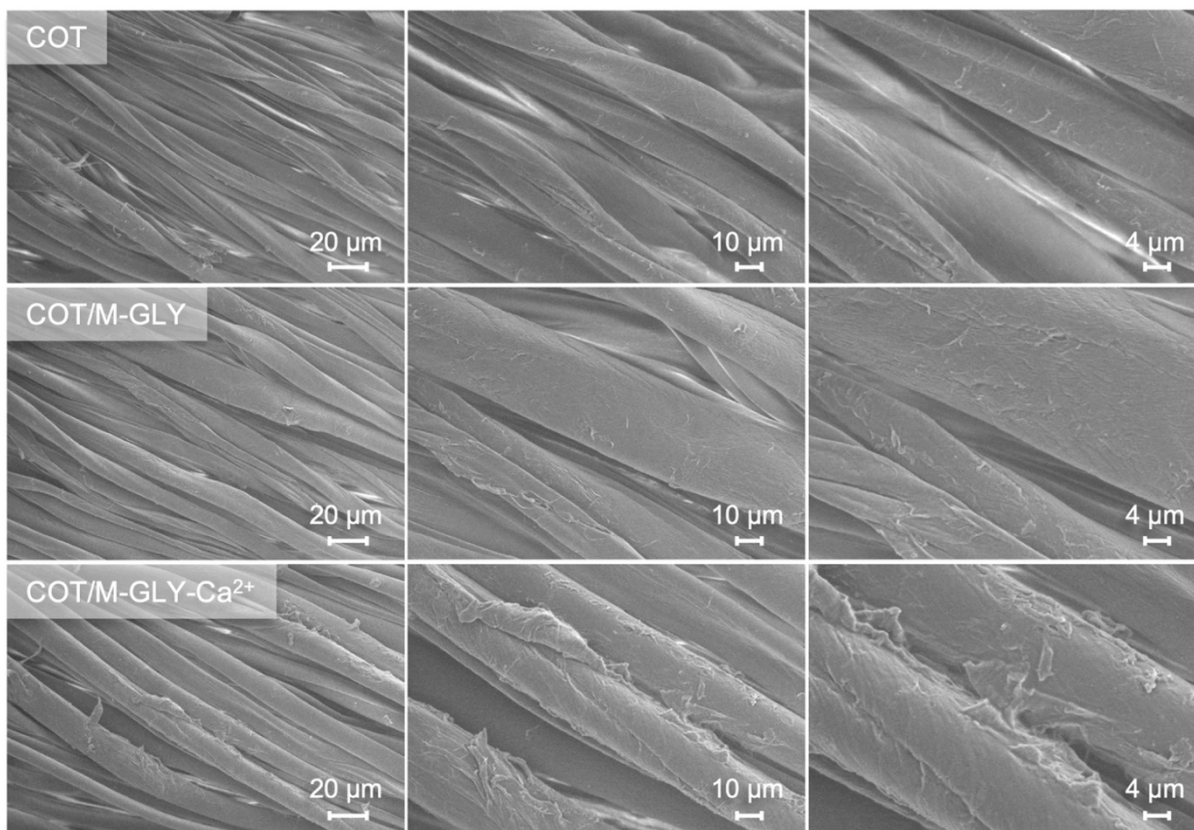
333 °C. ^{e)} COT/M-GLY add-on: 7%. ^{f)} COT/Ca²⁺ add-on: 2%. ^{g)} COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 7% M-GLY.

334 ^{b)} This value includes a 2% CaCl₂ residue.

335

336 3.6 Morphological characterization of M-GLY-Ca²⁺- and M-GLY-treated cotton fabrics

337 The surface morphologies of cotton fabrics treated with M-GLY-Ca²⁺ and M-GLY, whose
338 chemical structure was confirmed by FT-IR/ATR (Fig. S3), were assessed by SEM observations,
339 and compared with that of untreated cotton (Fig. 7). Both untreated and M-GLY-treated cotton
340 fabrics showed fibers characterized by smooth, flat surfaces that retained their individuality. In the
341 case of COT/M-GLY-Ca²⁺, the fiber surface appeared rougher. The element mapping obtained by
342 EDX analyses (Fig. 8) indicated a homogenous distribution of Ca²⁺ on cotton.



343

344 **Fig. 7.** SEM micrographs of untreated cotton (COT) and cotton fabrics treated with M-GLY and M-GLY-Ca²⁺.

345

COT/M-GLY add-on: 7%; COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 7% M-GLY.

346

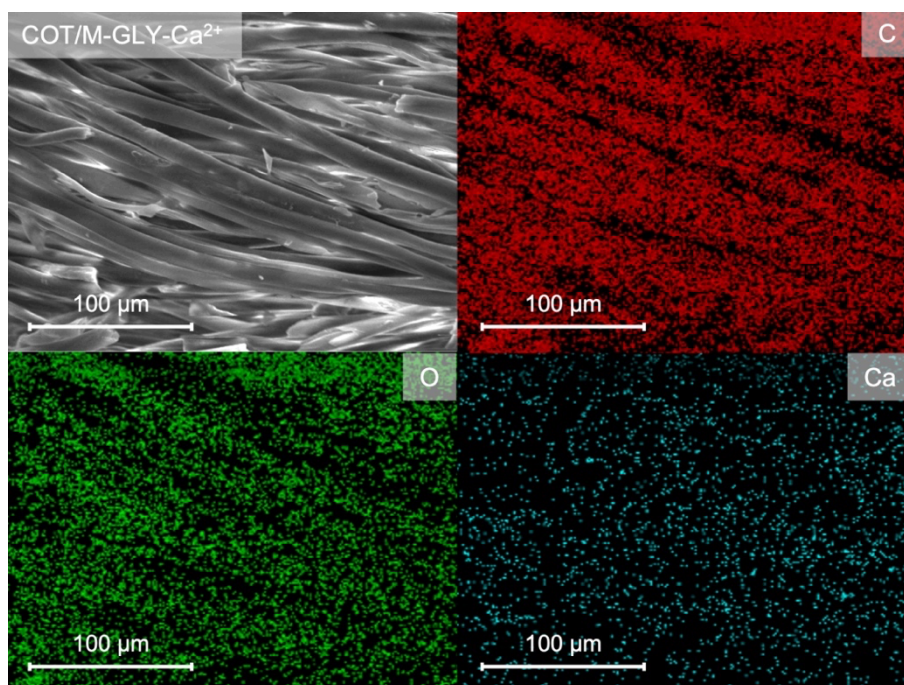


Fig. 8. EDX analysis of COT/M-GLY- Ca^{2+} ; distribution of carbon (C), oxygen (O), and calcium (Ca) elements.

347

348

349

3.7 Combustion of M-GLY- Ca^{2+} -treated cotton fabrics

3.7.1 Horizontal Flame Spread Tests (HFSTs)

The combustion behavior of M-GLY- Ca^{2+} -treated cotton fabrics in comparison with untreated and M-GLY-treated cotton fabrics was first assessed by horizontal flame spread tests, whose main results are reported in Table 3. Additionally, snapshots of the ignition and end-of-test phases are shown in Fig. 9 for COT/M-GLY- Ca^{2+} , COT/M-GLY, COT/ Ca^{2+} and untreated cotton. All HFSTs were carried out choosing a 7% add-on, which corresponds to the minimum add-on at which M-GLY had proved capable of imparting rapid self-extinguishment to cotton [16]. As noted earlier, COT/M-GLY burned only for 20 s in the presence of flame and stopped burning after 67 s afterglow, consuming a very small portion of sample, and leaving an RMF of 87% (Fig. 9, Table 3). The presence of CaCl_2 alone did not inhibit the combustion of cotton, which completely burned, but it slowed it down and promoted the formation of 16% RMF. The combination of M-GLY with CaCl_2 proved to be an even more effective protective coating than M-GLY, which in previous studies exhibited excellent performance in HFSTs. In fact, COT/M-GLY- Ca^{2+} burned for a shorter time, only 10 s and, after 51 s afterglow, left a slightly higher RMF: 90% vs. 87% for M-GLY- Ca^{2+} and M-GLY, respectively (Table 3). These results support the hypothesis of synergism between M-GLY and Ca^{2+} in protecting cotton fabrics by promoting char formation.

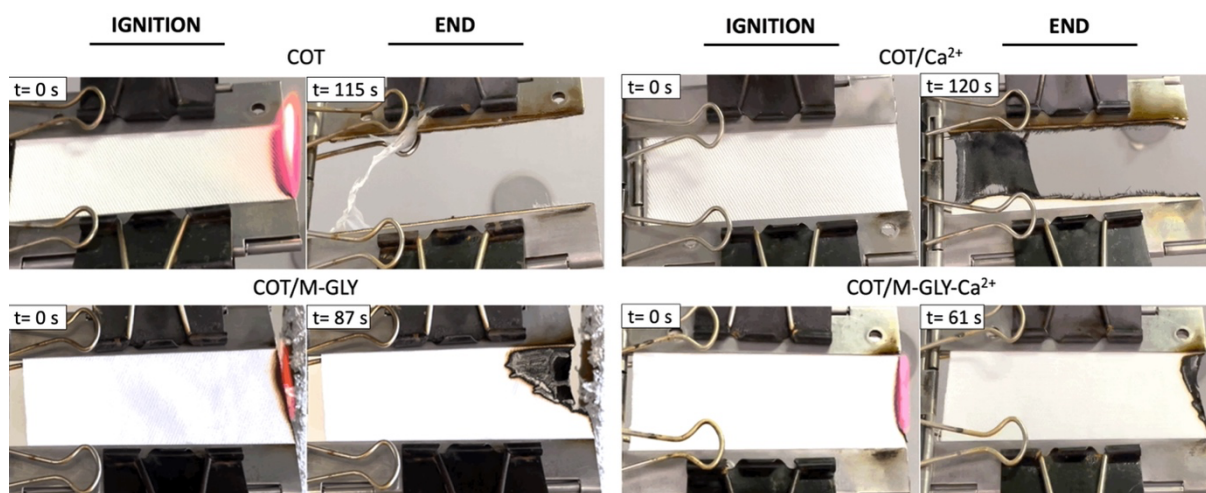
367 **Table 3**

368 Combustion data of M-GLY and M-GLY-Ca²⁺-treated cotton fabrics from horizontal flame spread tests.

Sample	Flaming combustion time ^{a)} (s)	Afterglow combustion time ^{a)} (s)	Extinguishment	RMF ^{b)} (%)
COT	80	35	NO	<1
COT/M-GLY ^{c)}	20	67	YES	87
COT/Ca ²⁺ ^{d)}	85	35	NO	16
COT/M-GLY-Ca ²⁺ ^{e)}	10	51	YES	90

^{a)} Combustion time ± 1 s. ^{b)} RMF ± 1.0%. ^{c)} COT/M-GLY add-on: 7%. ^{d)} COT/Ca²⁺ add-on: 2%. ^{e)} COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 7% M-GLY.

369



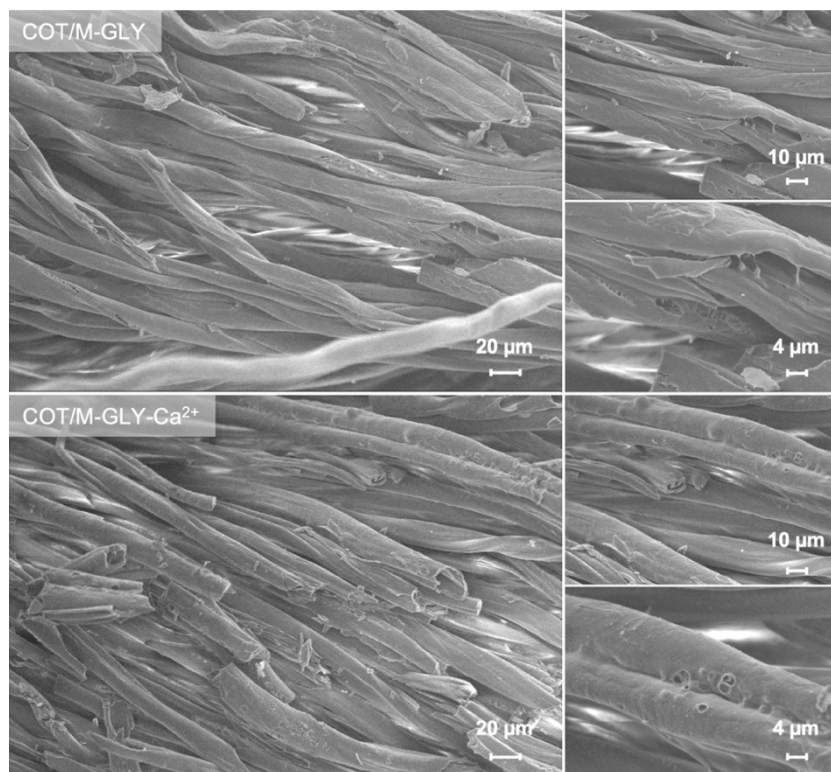
370

371 **Fig. 9.** Snapshots of horizontal flame spread tests for untreated cotton (COT) and cotton treated with M-GLY, Ca²⁺
372 and M-GLY-Ca²⁺. COT/M-GLY add-on: 7%; COT/Ca²⁺ add-on: 2%; COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 7%
373 M-GLY.

374

375 The burnt portion of the COT/M-GLY-Ca²⁺ and COT/M-GLY residues was observed by SEM
376 (Fig. 10). Despite combustion, the cotton texture was maintained in both cases, and the coating
377 was still intact, although the fibers were partially consumed inside. Noticeably, the surface of the
378 COT/M-GLY-Ca²⁺ coating showed some protuberances and partially exploded bubbles due to the
379 intumescence of M-GLY.

380



381
 382 **Fig. 10.** SEM micrographs of the chars present in the residues of cotton (COT) fabrics treated with M-GLY and M-
 383 GLY-Ca²⁺ at the end of HFSTs. COT/M-GLY add-on: 7%; COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 7% M-GLY.
 384

385 *3.7.2 Vertical Flame Spread Tests (VFSTs)*

386 The flame retardant performance of M-GLY-Ca²⁺ was assessed also in vertical configuration
 387 combustion tests, thus mimicking a more severe fire scenario. For this reason, it was necessary to
 388 increase the M-GLY add-on to 19% with respect to 7% used in HFSTs, while CaCl₂ add-on was
 389 maintained at 2%. Results were compared with those of cotton and COT/M-GLY (Table 4).
 390 Snapshots of the corresponding ignition and end-of-test phases for cotton, COT/M-GLY and
 391 COT/M-GLY-Ca²⁺ are shown in Fig. 11. In these tests, cotton burnt more rapidly than in HFSTs
 392 (80 s vs. 20 s in the presence of flame). M-GLY and CaCl₂ alone were not able to suppress cotton
 393 combustion, although both partially protected it, especially M-GLY, favoring char formation, as
 394 evidenced by the RMF values shown in Table 4. On the contrary, COT/M-GLY-Ca²⁺ did not ignite,
 395 but underwent a modest afterglow, consuming a small specimen area (Fig. 11) and leaving an RMF
 396 of 82% (Table 4).

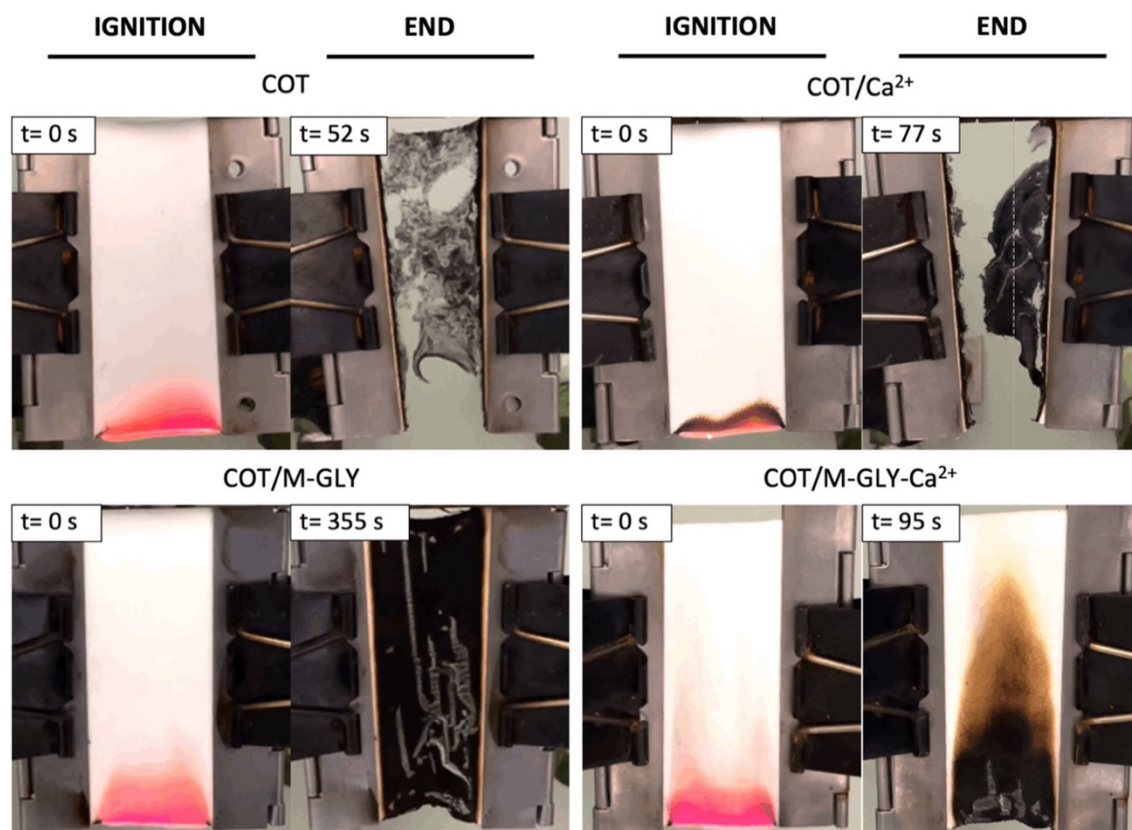
397
 398
 399

400 **Table 4**

401 Combustion data of M-GLY and M-GLY-Ca²⁺-treated cotton fabrics from vertical flame spread tests.

Sample	Flaming combustion time ^{a)} (s)	Afterglow combustion time ^{a)} (s)	Extinguishment	RMF ^{b)} (%)
COT	20	32	NO	<1
COT/M-GLY ^{c)}	15	340	NO	22
COT/Ca ²⁺ ^{d)}	12	65	NO	5
COT/M-GLY-Ca ²⁺ ^{e)}	5	90	YES	82

^{a)} Combustion time ± 1 s. ^{b)} RMF ± 1.0%. ^{c)} COT/M-GLY add-on: 19%. ^{d)} COT/Ca²⁺ add-on: 2%. ^{e)} COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 19% M-GLY.



402 **Fig. 11.** Snapshots of vertical flame spread tests for untreated cotton (COT) and cotton treated with M-GLY, CaCl₂
 403 and M-GLY-Ca²⁺. COT/M-GLY add-on: 19%; COT/Ca²⁺ add-on: 2%; COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and
 404
 405 19% M-GLY.

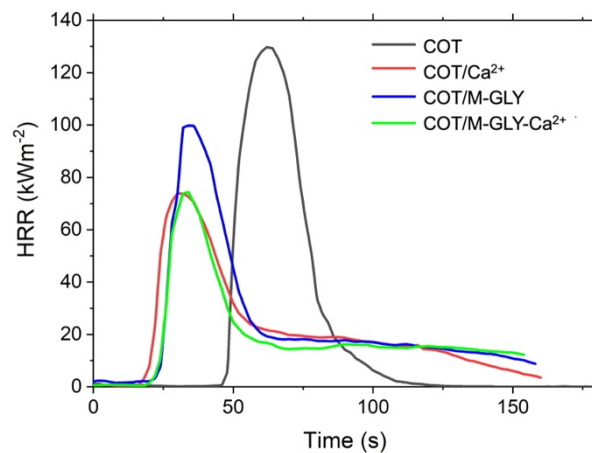
406 3.7.3 Oxygen-consumption cone calorimetry tests

407 Oxygen-consumption cone calorimetry tests were performed by exposing cotton fabrics treated
408 with M-GLY and M-GLY-Ca²⁺ to a 35 kWm⁻² heat flux. This experimental condition is usually
409 found in developing fires, capable of bringing the sample surface to about 520 °C [42]. Generally,
410 upon heating polymers undergo thermal oxidation, releasing combustible volatile gases that cause
411 polymer ignition and then combustion. Combustion parameters such as time to ignition (TTI), heat
412 release rate peak (pkHRR), total heat release (THR) and residual mass fraction (RMF) are reported
413 in Table 5, while Fig. 12 shows the heat release rate (HRR) curves of COT, COT/Ca²⁺, COT/M-
414 GLY, and COT/M-GLY-Ca²⁺.

415 M-GLY, CaCl₂ and M-GLY-Ca²⁺ significantly influenced cotton combustion. The TTI of cotton
416 was reduced by almost 50% in all cases. This can be ascribed to the anticipated formation of
417 thermally stable chars that protect cotton from combustion, reducing the pkHRR from 130 kWm⁻
418 ² to 108, 77 and 75 kWm⁻² for COT/M-GLY, COT/CaCl₂ and COTM-GLY-Ca²⁺, respectively (-
419 17%, -41% and -43%). CaCl₂ was found to be more efficient than M-GLY.

420 Interestingly, COT/M-GLY-Ca²⁺ exhibited an HRR curve almost superimposable to that of COT/
421 Ca²⁺ and, additionally, both pkHRR and THR values of COT/M-GLY-Ca²⁺ were significantly
422 lower than those of COT/M-GLY.

423



424

425 **Fig. 12.** Heat release rate curves of COT, COT/Ca²⁺, COT/M-GLY, and COT/M-GLY-Ca²⁺. COT/M-GLY add-on:
426 19%, COT/Ca²⁺ add-on: 2%, COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 19% M-GLY.

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Table 5
Combustion data of M-GLY and M-GLY-Ca²⁺-treated cotton fabrics from oxygen-consumption cone calorimetry.

Sample	TTI ^{a)} (s)	pkHRR ^{b)} (kWm ⁻²), (reduction, %)	THR ^{c)} (m ² m ⁻²)	RMF ^{d)} (%)
COT	50±3	130±2	3.3±0.4	1
COT/Ca ²⁺ ^{e)}	26±2	77±10 (-41%)	3.2±0.1	2
COT/M-GLY ^{f)}	25±2	108±2 (-17%)	3.8±0.1	1
COT/M-GLY-Ca ²⁺ ^{g)}	27±1	75±11 (-43%)	2.9±0.1	2

434 ^{a)} TTI: time to ignition. ^{b)} pkHRR: heat release rate peak. ^{c)} THR: total heat release. ^{d)} RMF: residual mass fraction. ^{e)}
435 COT/Ca²⁺ add-on: 2%. ^{f)} COT/M-GLY add-on: 19%. ^{g)} COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 19% M-GLY.

436

437 4. Conclusion

438 PAAs derived from the polyaddition of *N,N'*-methylenebisacrylamide with natural amino acids,
439 including the glycine-derived M-GLY, were previously shown to protect cotton fabrics from
440 combustion in horizontal flame spread tests due to their ability to give rise to intumescence. The
441 same PAAs, except for those derived from cystine, have not shown the same efficacy in vertical
442 flame spread tests. Since it has been recognized that metal ions improve the flame resistance of
443 cotton, it was thought to be worth studying whether combining M-GLY with CaCl₂ could increase
444 the efficacy of M-GLY as a flame retardant. The basic assumption was that Ca²⁺ ions could
445 establish intramolecular and ionic and Lewis acid/base interactions with the repeat units of M-
446 GLY and cellulose.

447 TG analysis in nitrogen and air of M-GLY/Ca²⁺ mixtures with the same composition as in the
448 protective coatings applied to cotton strips demonstrated that in both atmospheres the M-GLY-
449 Ca²⁺ adducts had much higher thermal stability than M-GLY, particularly above 500 °C. A
450 remarkable residual mass fraction was left by M-GLY-Ca²⁺ at 800 °C. This behavior has never
451 been observed in PAAs derived from amino acids. Not surprisingly, TG analysis demonstrated a
452 superior thermal stability of COT/M-GLY-Ca²⁺ compared to COT/M-GLY and COT/ Ca²⁺ in the
453 350-800 °C range in both nitrogen and air, showing synergism between M-GLY and CaCl₂ as
454 thermally protective coatings for cotton.

455 The performance as flame retardant of COT/M-GLY-Ca²⁺ in comparison with those of COT/M-
456 GLY and COT/Ca²⁺ were investigated in three different scenarios. In horizontal flame spread tests,

457 M-GLY-Ca²⁺ proved to be an even more effective protective coating than M-GLY, which in
458 previous studies exhibited excellent performance. In vertical flame spread tests, where M-GLY
459 failed to protect cotton even at add-ons >30%, M-GLY-Ca²⁺ proved very efficient in inhibiting
460 cotton ignition even at add-ons as low as 19% M-GLY and 2% CaCl₂, leaving an RMF of 82%.
461 No other PAA derived from natural amino acids, except those deriving from cystine one disulfide
462 group per repeat unit, have been found to be as efficient in vertical flame spread tests, even with
463 higher add-ons. In oxygen-consumption cone calorimetry tests, COT/M-GLY-Ca²⁺ showed a
464 remarkable pkHRR reduction as well a significant THR decrease, even higher than that of COT/M-
465 GLY.

466 Overall, the set of data collected in this work, prompt that the basic assumption of the establishment
467 of favorable interactions between Ca²⁺ ions and the repeat units of M-GLY and cellulose has been
468 confirmed. These promising results may open the way to the design of countless PAA-based hybrid
469 organic/inorganic flame retardant formulations for cotton.

470 It should be observed that the washing durability of the M-GLY/Ca²⁺ system is low, due to its
471 water solubility. However, the results reported here could be transferred to M-GLY-grafted cotton,
472 which represent the goal of this line of research [43].

473

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475 observations.

476

477 **Supplementary materials**

478 Supplementary material associated with this article can be found, in the online version, at doi:

479

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