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Use of calcium chloride to enhance the efficacy of polyamidoamines as flame retardants for cotton / Alongi, Jenny; Aad, Rony; Manfredi, Amedea; Carosio, Federico; Ferruti, Paolo; Ranucci, Elisabetta. - In: POLYMER DEGRADATION AND STABILITY. - ISSN 0141-3910. - ELETTRONICO. - 215:(2023). [10.1016/j.polymdegradstab.2023.110428]

Availability:

This version is available at: 11583/2985409 since: 2024-01-26T11:16:27Z

Publisher:

Elsevier

Published

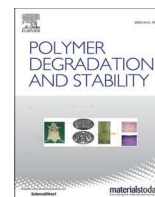
DOI:10.1016/j.polymdegradstab.2023.110428

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

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ARTICLE INFO

Keywords:

polyamidoamines
intumescent flame retardants
calcium chloride
functional coatings
cotton

ABSTRACT

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

1. Introduction

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

triazine-based FRs, UV-curable coatings, hybrid organic-inorganic FRs and polymeric additives, international regulations require more eco-compatible and non-toxic cotton FRs [6].

Polyamidoamines (PAAs) are multifunctional polymers synthesized by the aza-Michael polyaddition of *prim*- or *bis-sec*-amines, including natural α -amino acids with bis-acrylamides [7,8]. They can be synthesized in water at room temperature, pH 10 and with no added catalysts. Due to the type of polymerization, no by-products are formed. Many natural α -amino acid-derived PAAs are biocompatible [9,10] and, as suggested by recent studies, also eco-compatible [11]. Also polyamidoamines (PAAs) have recently proved to be considerably active as FRs for cotton, especially so those deriving from natural amino acids [12–18]. These PAAs proved non-flammable by applying a butane flame; intumescence occurred on their surface, which swelled and blackened, but the interior remained unaltered [16,17]. Solid state ¹³C nuclear magnetic resonance spectroscopy (NMR) coupled with X-ray photoelectron spectroscopy (XPS) clearly indicated that a glycine-derived PAA, coded M-GLY, promoted carbonization of cotton

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with formation of highly condensed aromatic structures, suggesting the existence of a nanographitic char [17]. Deposited on cotton, these PAAs extinguished the flame in horizontal flame spread tests (HFSTs) at add-ons as low as 4-7% [12], whereas most PAAs, including M-GLY, failed in vertical flame spread tests (VFSTs), with the only exception of the cystine-based polymers and glycine/cystine copolymers [15]. In all cases, the burnt cotton areas retained the original texture and showed intumescent microbubbles [12,17], as revealed by scanning electron microscopy (SEM). In oxygen consumption cone calorimetry tests, amino acid-derived PAAs increased the resistance of cotton to a 35 kWm⁻² irradiative heat flux, which is normally found in developing fires. They also reduced the heat release rate peak and the production of carbon oxides, leaving over 80% intact residual mass fraction. No smoke release was observed in these tests. Thermogravimetric analyses (TGA) showed that amino acid-derived PAAs sensitized cotton to thermal decomposition and intumesced when heated in air at 350 - 450°C, the temperature range where cotton undergoes thermo-oxidation.

It has been widely demonstrated that inorganic salts influence the thermal decomposition pathway of cellulose [19–29]. They generally reduce both the onset decomposition temperature and the maximum weight loss temperature and influence the distribution of the decomposition products. In their presence, cellulose preferentially undergoes dehydration rather than depolymerization [24,25] generating thermally stable aromatic chars [26–28]. The effect of inorganic salts has been ascribed to their ionic nature and their Lewis acidity or basicity strength on which the ability to stabilize specific reaction intermediates depends [19]. Furthermore, studies carried out with water insoluble Zn- and Co-ethylhexanoates demonstrated that also these organic salts increased char formation at 600°C [22]. The presence of ethylhexanoic acid in the pyrolyzed gases suggested the occurrence of an exchange reaction between the metal ions and the hydrogens of the cellulose hydroxyl groups. Concerning the effect of Ca²⁺, it has been reported that increasing amounts of CaCl₂ shifted progressively the entire thermal decomposition pattern earlier and led to increasing char residues at 800°C [23]. In fact, in a previous paper, it had been hypothesized that Ca²⁺ interact with the hydroxyl groups of the glycosidic monomeric unit of cellulose, therefore promoting dehydration and fragmentation, which represent a prelude to char formation, instead of producing levoglucosan and other depolymerization fragments [21]. Fast pyrolysis tests of cellulose in the presence of MgCl₂ and NaCl confirmed that both salts enhanced the ring opening of the pyranose residues above 250°C [29].

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

Based on this premise, it was thought it will be interesting to ascertain whether Ca²⁺ could influence the thermal-oxidative stability of amino acid-derived PAAs and of PAA-impregnated cotton by establishing ionic interactions with the carboxylate pendants or Lewis acid/base interactions with the amide C=O present in the repeat units of these PAAs and, furthermore, if these interactions could improve the PAA flame retardant activity. To this aim, in this work we have investigated in detail the performance of CaCl₂-based formulations of the glycine-derived PAA named M-GLY, which failed to quench combustion in vertical flame spread tests, which are the most realistic fire tests for textiles, even at add-on higher than 30%.

2. Experimental part

2.1. Materials

Glycine (GLY, >98%), *N,N'*-methylenebisacrylamide (M, 99%), lithium hydroxide monohydrate (LiOH·H₂O, 98%), calcium chloride

(CaCl₂, >97%), hydrochloric acid (HCl, 37% w/w aqueous solution) and deuterium oxide (D₂O, 99.9%) were purchased from Sigma-Aldrich (Milano, Italy) and used as received. Aqueous solutions were prepared using deionized water obtained with a Q20 Millipore system. Cotton fabric (COT) having an area density of 200 gm⁻² was purchased from Fratelli Ballezio S.r.l. (Torino, Italy).

2.2. Characterization techniques

The thermal and thermal-oxidative stability of M-GLY, M-GLY-Ca²⁺- and M-GLY-Ca²⁺-treated cotton fabrics were evaluated by thermogravimetric analysis (TGA) from 50 to 800°C with heating rate 10°C min⁻¹. A Perkin Elmer thermogravimetric balance, TGA 7 - Thermogravimetric Analyzer, was used, placing samples (5 mg) in open platinum pans, in either nitrogen or air under 20 mL min⁻¹ gas flow (Perkin Elmer, Milano, Italy). The surface morphologies of untreated and PAA-treated cotton, and combustion residues were characterized using an EVO 15 equipped with a ULTIM MAX 40 probe scanning electron microscope (SEM) (Zeiss, Ramsey, NJ, USA), operating at 8.5 mm working distance, under 5 kV beam voltage, equipped with Energy-Dispersive X-ray Spectroscopy (EDX, Jena, Germany) to perform elemental analyses. Small square samples of unburnt or burnt fabrics (5 mm x 5 mm) were fixed to the sample holder through conductive adhesive tapes and then gold metalized.

2.3. Synthesis of glycine-derived polyamidoamine

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

2.4. Impregnation of cotton fabrics

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

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

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

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

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

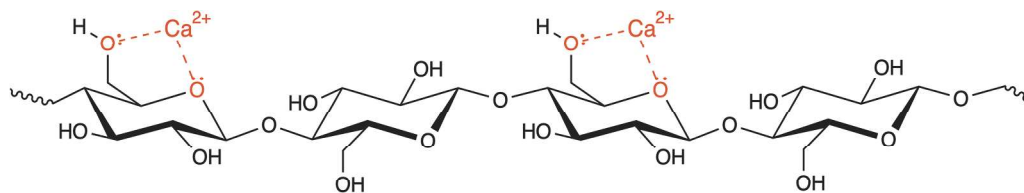


Fig. 1. Interaction of cellulose with Ca^{2+} ions [19].

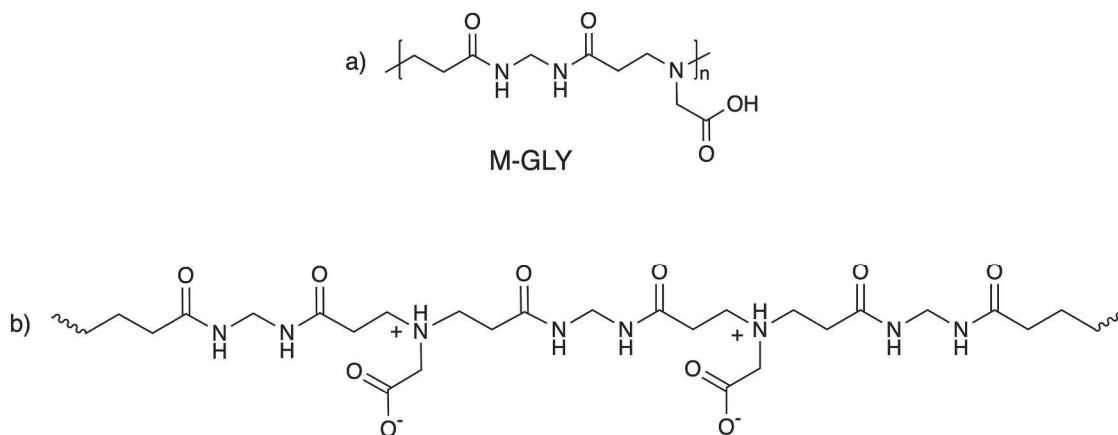


Fig. 2. M-GLY repeat unit: structure (a) and pH-dependent ionic species distribution (b).

2.5. Combustion tests

The ignitability of M-GLY (350 mg) and of a M-GLY/ CaCl_2 mixture (350 mg of M-GLY and 25 mg of CaCl_2) was assessed by applying a butane flame of 20 mm length for 20 s to the powdered sample placed on a porcelain surface. The M-GLY/ CaCl_2 mixture was obtained by grinding together the two components in a pestle and mortar to ensure homogeneous dispersion. Before testing, the specimens were conditioned at $27 \pm 1^\circ\text{C}$ and 50% relative humidity in a climate chamber until constant weight. All experiments were performed in duplicate.

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

The resistance to a 35 kWm^{-2} irradiative heat flux of square fabric samples (100 mm x 100 mm) was investigated using an oxygen-consumption cone calorimeter (Noselab Ats Srl, Bovisio-masciago, Monza-Brianza, Italy). Measurements were carried out in horizontal configuration, following a procedure previously reported [37] based on the ISO 5660 standard [38]. Parameters such as time to ignition (TTI, s), heat release rate peak (pkHRR , kWm^{-2}), total heat release (THR,

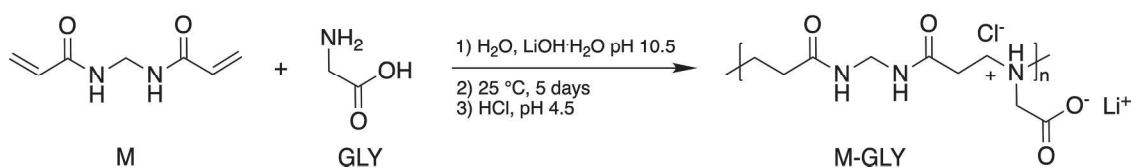
MJm^{-2}) and residual mass fraction (RMF, wt.-%) were determined. Prior to the combustion tests, all specimens were conditioned to constant weight at $23 \pm 1^\circ\text{C}$ for 48 h at 50% relative humidity in a climatic chamber. Each experiment was performed in triplicate and the standard deviation calculated.

3. Results and discussion

3.1. Rationale

In previous articles it has been hypothesized that Ca^{2+} ions, which are good Lewis acids [39], can interact with both the ether and the hydroxyl groups of cellulose pyranose ring (Fig. 1), promoting the homolytic cleavage of the covalent bonds of the pyranose ring [19]. This thermal decomposition pattern explains the formation of low molecular weight decomposition products including, among others, glycolaldehyde, acetol, and formic, and compete with the heterocyclic cleavage of the glycosidic linkages resulting in depolymerization and release of levoglucosan.

The glycine-derived PAA coded M-GLY (Fig. 2a), bearing in its repeat unit a *tert*-amine group and a carboxyl pendant, is a water-soluble amphoteric polymer with isoelectric point 4.8. At pH 5.0, at which the M-GLY is deposited onto cotton, its repeat units bear approximately 100% protonated *tert*-amine groups in the backbone (*tert*-amine $\text{pK}_a = 7.7$) and 100% carboxylate pendants (COOH $\text{pK}_a = 1.9$) (Fig. 2b). The relative amount of these two ionizable groups obviously change with pH, although the carboxyl pendants are always present in the deprotonated form in a wide pH range. Due to the presence of lithium carboxylate (Scheme 1) and secondary amide groups in all M-GLY repeat units,



Scheme 1. Synthesis of M-GLY.

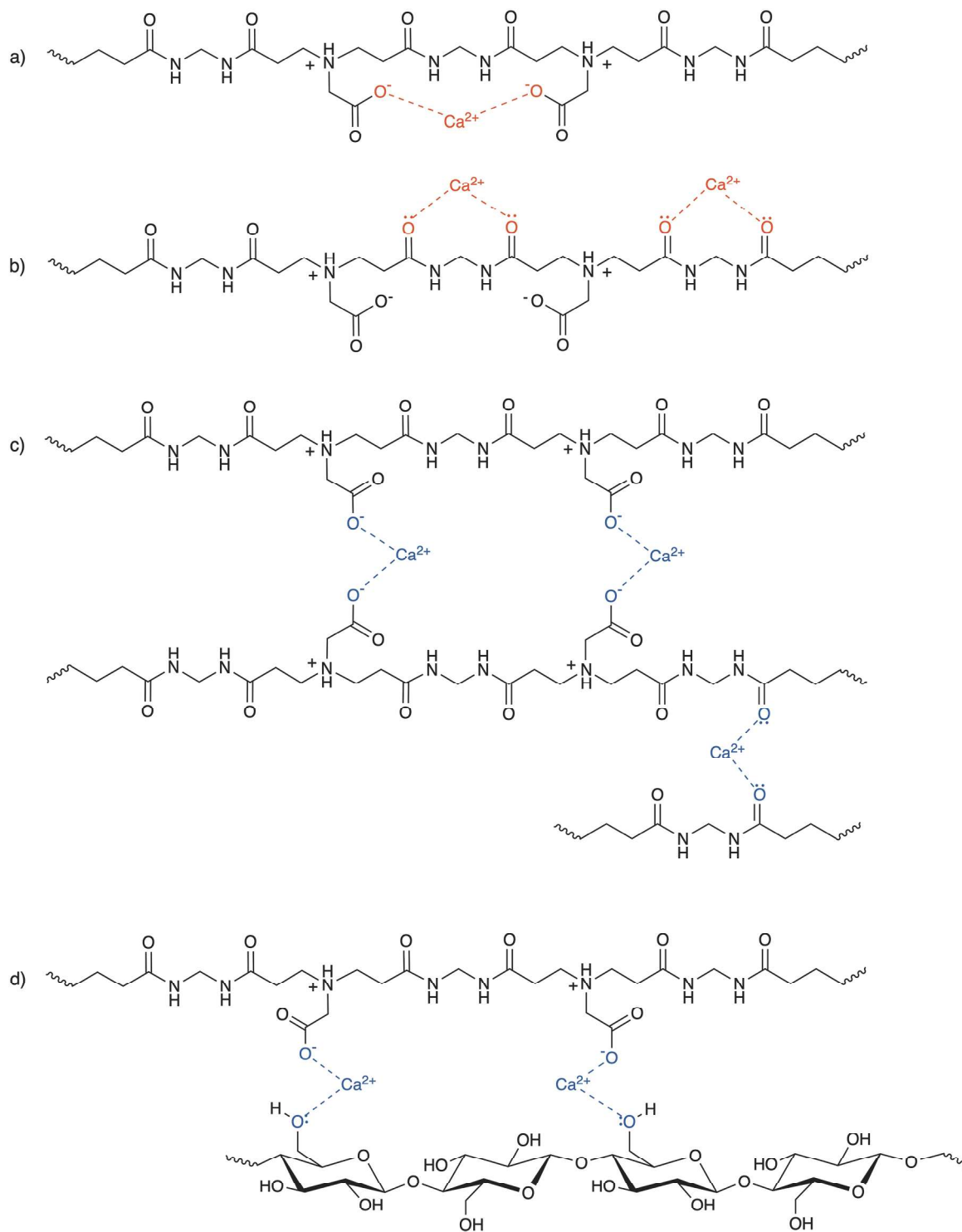


Fig. 3. Examples of possible intramolecular and intermolecular ionic and Lewis acid/base interactions of Ca^{2+} ions with the repeat units of M-GLY and cellulose: intramolecular M-GLY/ Ca^{2+} interactions (in red **a,b**); intermolecular M-GLY/ Ca^{2+} interactions (in blue **c**); intermolecular M-GLY/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

Ca^{2+} ions can give rise to intra- or inter-molecular ionic exchange reactions, as well as Lewis acid/base interactions with the amide $\text{C}=\text{O}$ groups (Fig. 3a-c). Furthermore, Ca^{2+} ions can act as a bridge between M-GLY and cellulose by exploiting different ionic and Lewis acid/base interactions (Fig. 3d). The aim of this work is to investigate the effect of this set of interactions on the thermal-oxidative stability of cotton fabrics coated with both M-GLY and CaCl_2 and, particularly, if these may give rise to synergistic actions.

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

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

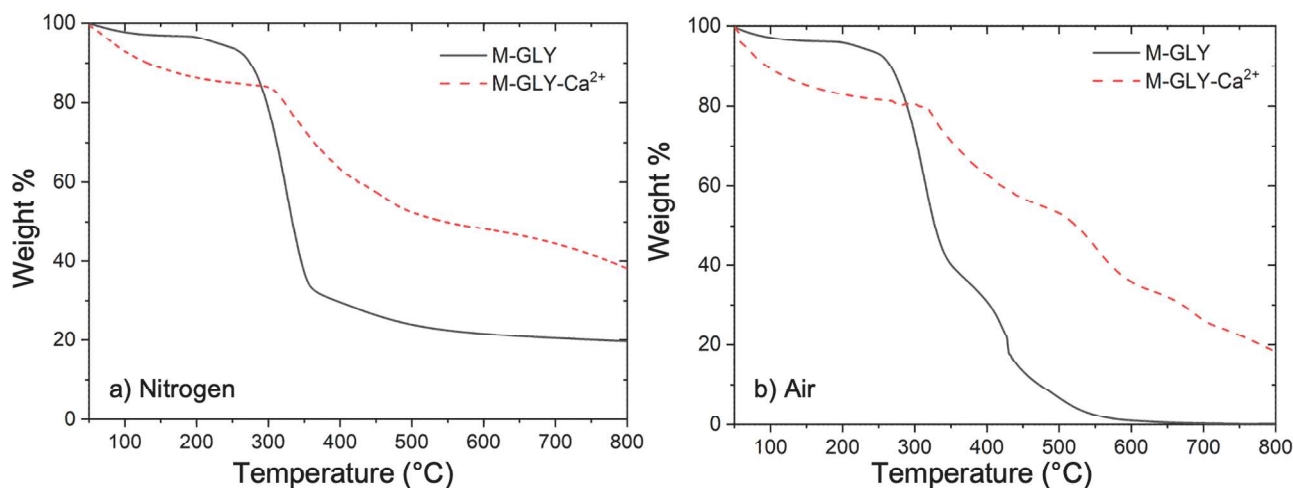


Fig. 4. TG thermograms of M-GLY-Ca²⁺ and M-GLY in nitrogen (a) and in air (b). The 3.5:1 M-GLY/CaCl₂ ratio (w/w) in M-GLY-Ca²⁺ is the same used in HFSTs.

Table 1

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 ^{d)}
<i>Air</i>				
M-GLY	267	310	428	0
M-GLY-Ca ²⁺ ^{e)}	162	320	430	19.0 ^{d)}

a) Onset decomposition temperature at 10% weight loss.

b) First temperature at maximum weight loss rate obtained from the derivative thermogravimetric curve of Fig. S4a and Fig. S4b.

c) Second temperature at maximum weight loss rate obtained from the derivative thermogravimetric curve of Fig. S4a and Fig. S4b.

d) Residual mass fraction at 800°C.

e) 3.5:1 M-GLY/CaCl₂ ratio (w/w).

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

The interaction mode of the Ca²⁺ ions with the M-GLY was investigated by means of FT-IR (Fig. S2a). The spectrum of the M-GLY-Ca²⁺ system, compared with those of M-GLY and CaCl₂, showed significant changes with respect to those of M-GLY and CaCl₂ alone in well-defined spectral ranges. In particular, the IR spectrum of M-GLY exhibited two diagnostic peaks placed at 1626 and 1529 cm⁻¹. The first is due to the overlapping of the carboxylate stretching band and the so-called amide I band, the second to the amide II band. It is apparent that in the M-GLY-Ca²⁺ system the amide II band, that is, the amide N-H bending, reduced and broadened significantly, whereas a new narrow band appeared at 1613 cm⁻¹ (Fig. S2b). This change can be attributed to the interaction of the Ca²⁺ ions with the amide C=O groups, which alters the strength of the hydrogen bond involving the amide N-H and causes a shift to higher wavenumbers. This peculiar effect of the Ca²⁺ interaction with the amide groups of polymers has been already reported, *inter alia*, in the case of PA6,6 [40]. Not unexpectedly, the carboxylate stretching band did not apparently shift following the lithium/calcium ion exchange. A second relevant change involving the vibrational mode of the N-H group was observed in the 3000-3500 cm⁻¹ spectral region, where M-GLY exhibited a broad band due to the amide N-H stretching, which converted into a narrow bimodal band centered at 3442 and 3493 cm⁻¹. It can be finally observed that the Ca-Cl band placed in pure CaCl₂ at 649 cm⁻¹ [41] disappeared in the spectrum of the spectrum of the M-GLY-Ca²⁺ system.

3.3. Thermal stability of M-GLY-Ca²⁺ and M-GLY

Fig. 4 shows the TG thermograms between 50 and 800°C both in nitrogen and in air of a 3.5:1 (w/w) homogeneous M-GLY/CaCl₂ mixture, coded as M-GLY-Ca²⁺, and M-GLY. The selected M-GLY/CaCl₂ weight ratio is the same as the mixture applied on cotton fabrics in horizontal flame spread tests (section 2.4). The relevant thermal data are collected in Table 1. To ensure the most even distribution of the two components, the M-GLY-Ca²⁺ mixture was prepared by dissolving in water M-GLY and CaCl₂ in suitable amounts and then freeze-drying the resultant mixed solution. It should be observed that in Fig. 4 the thermogram of CaCl₂ is not shown, since it is known that in anhydrous conditions CaCl₂ dehydrates in between 180 - 260°C, and then is stable up to around 800°C [40].

Consistent with previous findings [12], in nitrogen M-GLY mainly decomposed in between 250-350°C with an overall weight loss of about 65% (Fig. 4a). The residue formed at 350°C slowly decomposed at higher temperatures, until leaving a residual mass fraction at 800°C, RMF₈₀₀, of 20.0% (Table 1). In M-GLY-Ca²⁺, the presence of Ca²⁺ induced M-GLY dehydration at a lower T_{onset10%} (Fig. 4a, Table 1), while shifting the onset of thermal decomposition to 300°C, *i.e.*, by 50°C higher than for M-GLY alone. The residue formed at 300°C underwent further slow decomposition between 300 and 800°C, an interval within which two maximum weight loss temperatures were identified, namely T_{max1} = 344°C and T_{max2} = 550°C. Additionally, M-GLY-Ca²⁺ left a significantly higher RMF₈₀₀ compared to M-GLY (37.0% including a 2% CaCl₂ residue vs. 20.0%).

In air, both M-GLY-Ca²⁺ and M-GLY showed multimodal weight loss curves (Fig. 4b). In detail, M-GLY decomposed through a two-step pathway, with a first weight loss from 250 to 350°C of about 50%, *i.e.*, significantly lower than in nitrogen. Overall, the TG trace of M-GLY in air showed a significantly lower weight loss in the whole 300-570°C temperature range than in nitrogen, due to the well-known intumescent behavior of this polymer, which generated in air an expanded carbonaceous char [12,17]. This char further oxidized at higher temperatures until leaving an almost negligible RMF₈₀₀ (Table 1). In air, M-GLY-Ca²⁺ was significantly more stable than in nitrogen and much more stable than M-GLY in air. In the latter environment, three main weight phenomena were observed in the 320-800°C range: a first weight loss of only about 30% in between 320-450°C, a second weight loss of 30% in the 450-550°C range, and a slow oxidation from 550°C upward until an RMF₈₀₀ of about 19%, including a 2% CaCl₂ residue (Table 1). Such a high thermal stability in air over a wide temperature range (from 300 to 800°C), associated with a residual mass fraction at 800°C of 19% have never been observed in PAAs and represent an exceptional result. The set

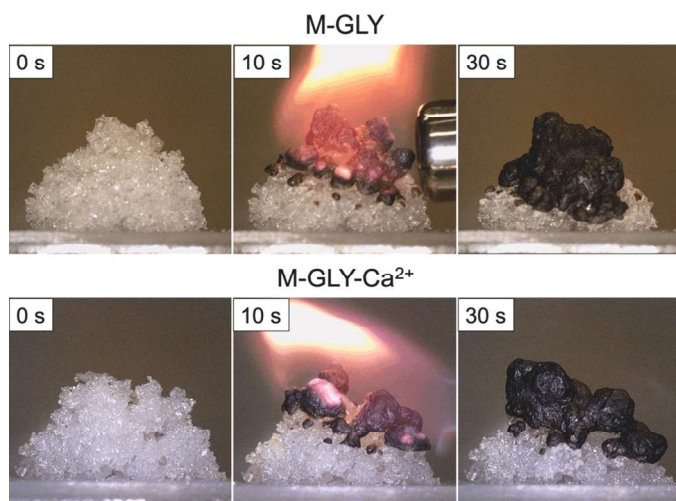


Fig. 5. Snapshots of the ignitability tests of M-GLY and M-GLY-Ca²⁺.

of data collected suggests that CaCl₂ has a stabilizing effect on M-GLY. This might be ascribed to the establishment of intermolecular and/or intramolecular interactions, either ionic or Lewis acid/base interactions, between Ca²⁺ ions and the functional groups present in the M-GLY repeat units (Fig. 3a-c).

3.4. Ignitability of M-GLY-Ca²⁺ and M-GLY

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

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

The TG thermograms of M-GLY-Ca²⁺-treated cotton with 7% M-GLY add-on and 2% CaCl₂ add-on obtained from 50 to 800°C in nitrogen and in air were compared with those of cotton treated with either M-GLY (add-on 7%) or CaCl₂ (add-on 2%), and with those of untreated cotton (Fig. 6). The relevant thermal data are collected in Table 2. Overall, CaCl₂, M-GLY and M-GLY-Ca²⁺ sensitized the thermal decomposition of

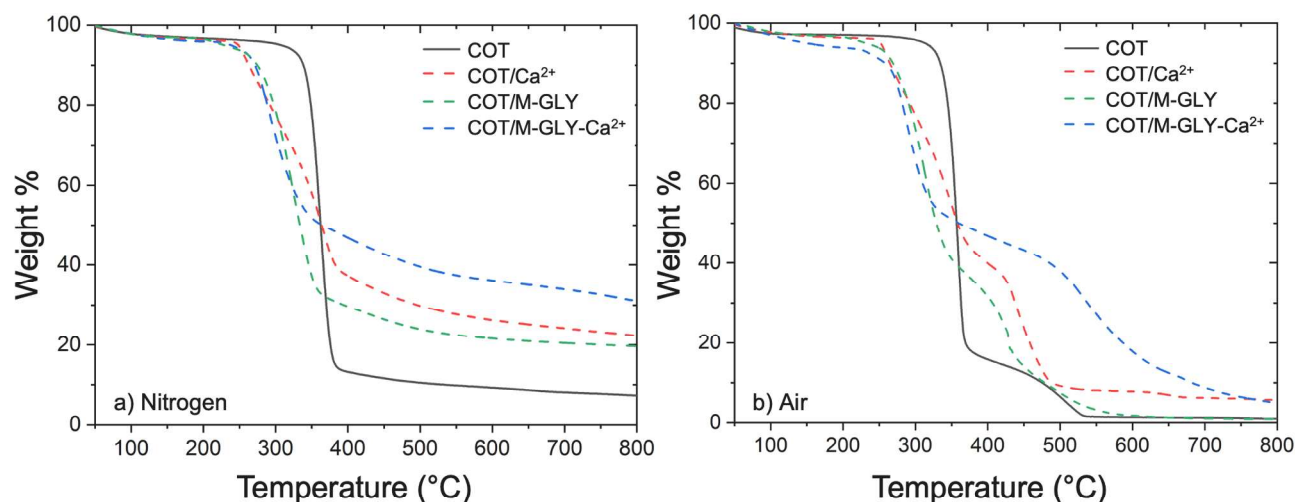


Fig. 6. TG thermograms of untreated cotton (COT), and Ca²⁺-, M-GLY-, M-GLY-Ca²⁺-treated cotton fabrics in nitrogen (a) and air (b). COT/M-GLY add-on: 7%; COT/Ca²⁺ add-on: 2%; COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 7% M-GLY.

cotton by reducing the $T_{\text{onset}10\%}$ values in both atmospheres, while significantly increasing the residue formation at $T > 400^\circ\text{C}$, although with qualifications [34]. In nitrogen, after the first weight loss, untreated cotton left an RMF of about 10%, at around 380°C, while M-GLY- and Ca²⁺-treated cotton left an RMF of about 30% and 38%, respectively, at around 350°C. Noticeably, M-GLY-Ca²⁺-treated cotton left an RMF of about 55% at 350°C (including a 2% CaCl₂ residue), i.e., by far higher than those left by cotton treated with M-GLY and CaCl₂ alone (Fig. 6a). Above 350°C, the chars further decomposed leaving in all cases particularly high RMF₈₀₀ values, specifically for COT/M-GLY-Ca²⁺ (31.0%, including a 2% CaCl₂ residue, Table 2).

In air, the thermal stability of the coated cotton samples was much higher than that of untreated cotton, particularly in the range 350–450°C for COT/Ca²⁺ and COT/M-GLY, within which PAAs normally undergo significant intumescence [17], and in the range 350–650°C for COT/M-GLY-Ca²⁺ (Fig. 6b). Additionally, the fact that above 550°C the residual mass values of COT/M-GLY-Ca²⁺ (30% including 2% CaCl₂ residue) are much higher than the sum of those of COT/Ca²⁺ and COT/M-GLY (8% and 1%, respectively) is a clear indication that M-GLY and CaCl₂ act synergically as thermally protective coating of cotton. This is most likely due to the intramolecular and/or intermolecular ionic and Lewis acid/base interactions between M-GLY and Ca²⁺ (Fig. 3a-c) and/or to the concomitant presence of intermolecular M-GLY-/Ca²⁺/cellulose interactions (Fig. 3d).

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

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

3.7. Combustion of M-GLY-Ca²⁺-treated cotton fabrics

3.7.1. Horizontal Flame Spread Tests (HFSTs)

The combustion behavior of M-GLY-Ca²⁺-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

Table 2

Thermal data of M-GLY-Ca²⁺- and M-GLY-treated cotton fabrics in nitrogen and air by 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)}

^{a)} Onset decomposition temperature at 10% weight loss. ^{b)} First temperature at maximum weight loss rate obtained from the derivative thermogravimetric curve of Fig. S4c and Fig. S4d. ^{c)} Second temperature at maximum weight loss rate obtained from the derivative thermogravimetric curve of Fig. S4c and Fig. S4d. ^{d)} Residual mass fraction at 800°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. ^{h)} This value includes a 2% CaCl₂ residue.

phases are shown in Fig. 9 for COT/M-GLY-Ca²⁺, COT/M-GLY, COT/Ca²⁺ 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 CaCl₂ 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 CaCl₂ 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-Ca²⁺ burned for a shorter time, only 10 s and, after 51 s afterglow, left a slightly higher RMF: 90% vs. 87% for M-GLY-Ca²⁺ and M-GLY,

respectively (Table 3). These results support the hypothesis of synergism between M-GLY and Ca²⁺ in protecting cotton fabrics by promoting char formation.

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

3.7.2. Vertical Flame Spread Tests (VFSTs)

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

3.7.3. Oxygen-consumption cone calorimetry tests

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

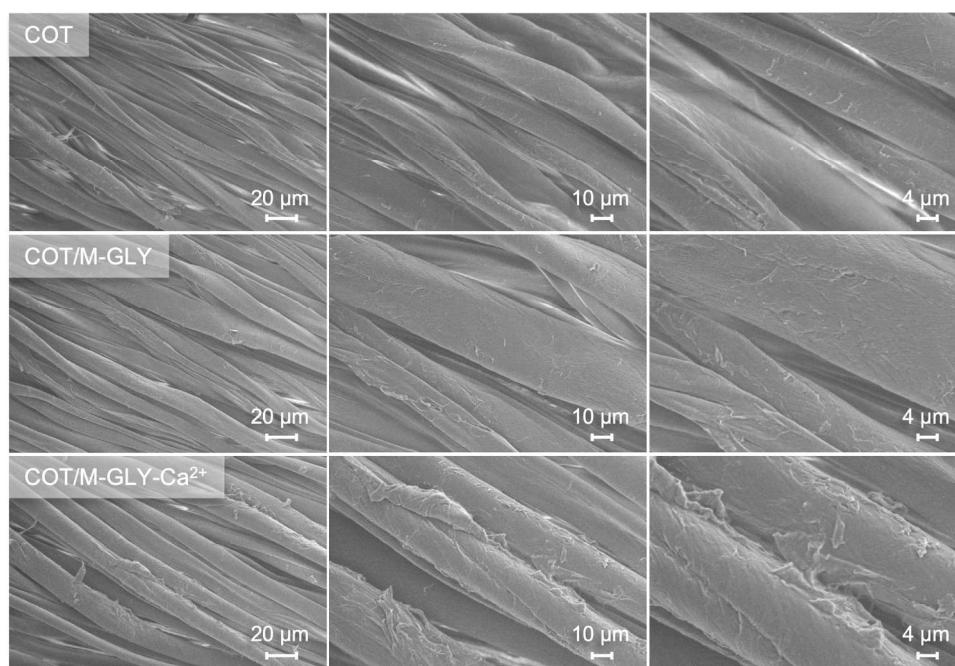


Fig. 7. SEM micrographs of untreated cotton (COT) and cotton fabrics treated with M-GLY and M-GLY-Ca²⁺. COT/M-GLY add-on: 7%; COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 7% M-GLY.

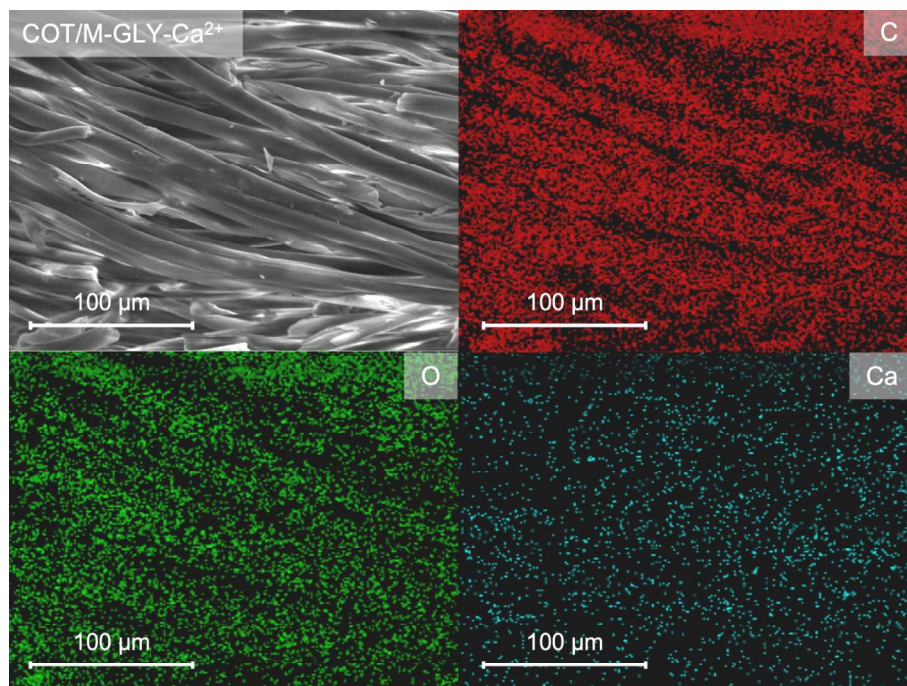


Fig. 8. EDX analysis of COT/M-GLY-Ca²⁺; distribution of carbon (C), oxygen (O), and calcium (Ca) elements.

Table 3

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.

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

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

4. Conclusion

PAAAs derived from the polyaddition of *N,N'*-methyl-enebisacrylamide with natural amino acids, including the glycine-

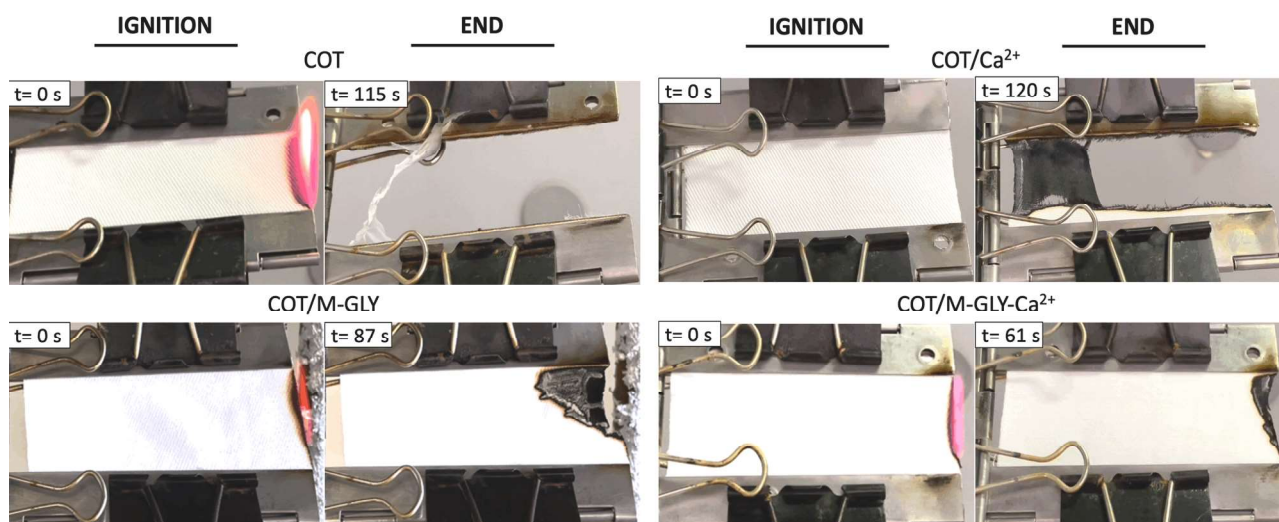


Fig. 9. Snapshots of horizontal flame spread tests for untreated cotton (COT) and cotton treated with M-GLY, Ca²⁺ and M-GLY-Ca²⁺. COT/M-GLY add-on: 7%; COT/Ca²⁺ add-on: 2%; COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 7% M-GLY.

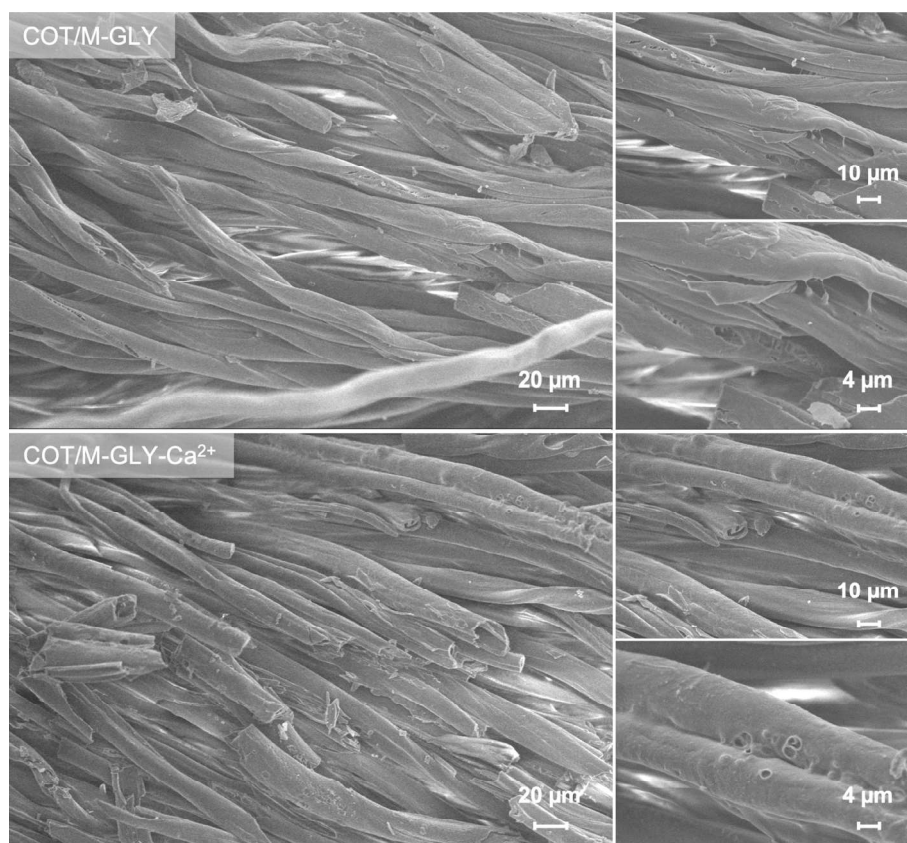


Fig. 10. SEM micrographs of the chars present in the residues of cotton (COT) fabrics treated with M-GLY and M-GLY-Ca²⁺ at the end of HFSTs. COT/M-GLY add-on: 7%; COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 7% M-GLY.

Table 4

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 \pm 1 s. ^{b)} RMF \pm 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.

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

TG analysis in nitrogen and air of M-GLY/Ca²⁺ mixtures with the same composition as in the protective coatings applied to cotton strips demonstrated that in both atmospheres the M-GLY-Ca²⁺ adducts had much higher thermal stability than M-GLY, particularly above 500°C. A remarkable residual mass fraction was left by M-GLY-Ca²⁺ at 800°C.

This behavior has never been observed in PAAs derived from amino acids. Not surprisingly, TG analysis demonstrated a superior thermal stability of COT/M-GLY-Ca²⁺ compared to COT/M-GLY and COT/Ca²⁺ in the 350–800°C range in both nitrogen and air, showing synergism between M-GLY and CaCl₂ as thermally protective coatings for cotton.

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

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

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

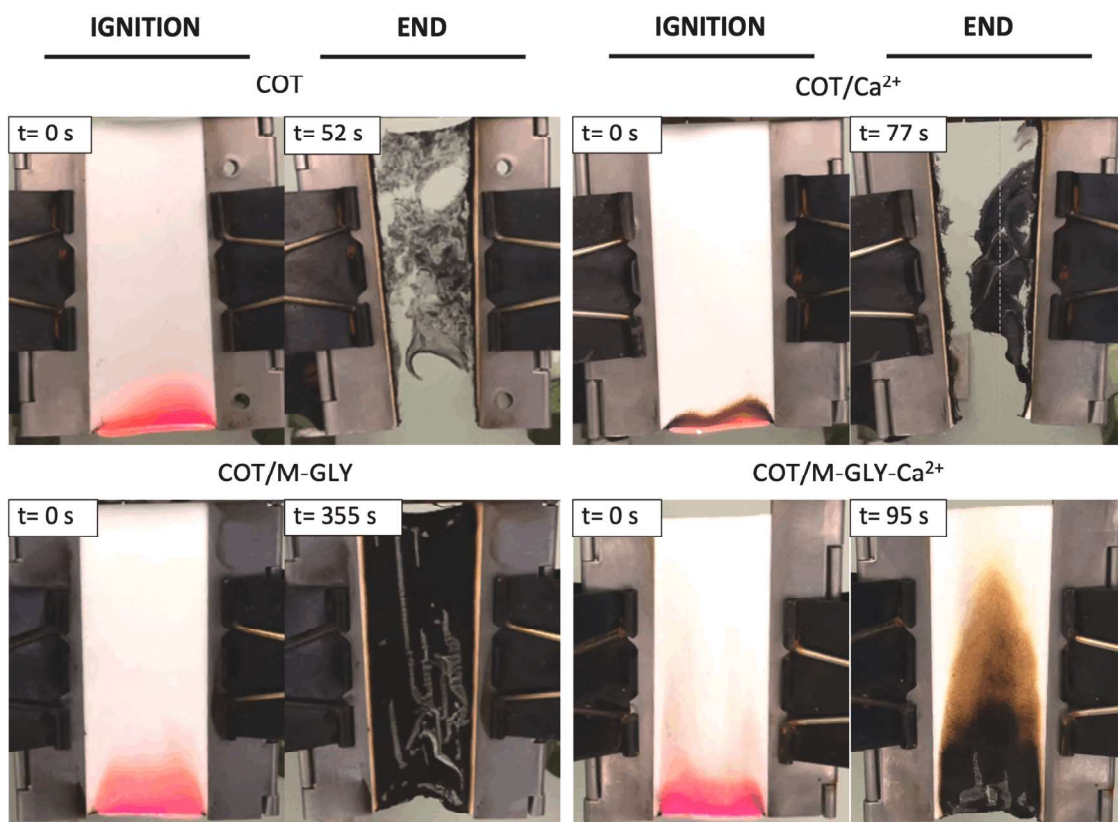


Fig. 11. Snapshots of vertical flame spread tests for untreated cotton (COT) and cotton treated with M-GLY, CaCl₂ and M-GLY-Ca²⁺. COT/M-GLY add-on: 19%; COT/Ca²⁺ add-on: 2%; COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 19% M-GLY.

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

a) TTI: time to ignition.

b) pkHRR: heat release rate peak.

c) THR: total heat release.

d) RMF: residual mass fraction.

e) 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.

CRedit authorship contribution statement

Jenny Alongi: Methodology, Writing – review & editing, Supervision. **Rony Aad:** Investigation, Methodology. **Amedea Manfredi:** Methodology, Writing – review & editing. **Federico Carosio:** Investigation, Methodology. **Paolo Ferruti:** Conceptualization, Writing – original draft, Supervision. **Elisabetta Ranucci:** Conceptualization, Writing – original draft, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

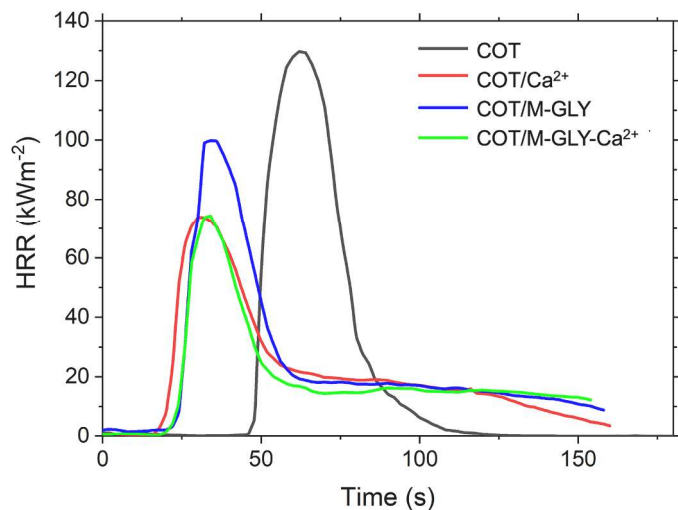


Fig. 12. Heat release rate curves of COT, COT/Ca²⁺, COT/M-GLY, and COT/M-GLY-Ca²⁺. COT/M-GLY add-on: 19%, COT/Ca²⁺ add-on: 2%, COT/M-GLY-Ca²⁺ add-on: 2% CaCl₂ and 19% M-GLY.

Data availability

The data that has been used is confidential.

Acknowledgments

The authors greatly thank D. Pezzini (Politecnico di Torino) for the SEM observations.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.polydegradstab.2023.110428](https://doi.org/10.1016/j.polydegradstab.2023.110428).

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