Linear Polyamidoamines as Novel Biocompatible Phosphorus-Free Surface-Confined Intumescent Flame Retardants for Cotton Fabrics

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Abstract: Eight linear polyamidoamines (PAAs) prepared by polyaddition of amines to bisacrylamides are investigated as intumescent surface-confined flame retardants for cotton textiles. The structure of the amine-derived subunits governs their performances. In ignitability tests, aminoacid-deriving PAAs exposed to direct flame for 10 s do not burn, but produce carbonaceous crusts sheltering the underneath sample apparently intact. PAAs carrying guanidine pendants partially volatilize without burning. 2-Methylpiperazine-derived PAAs burn completely. Thermogravimetric analyses show that in air at ≥400 °C all PAAs leave substantial char residues that oxidize at >500 °C. Horizontal flame spread tests on PAA-impregnated cotton stripes show flame extinction for add-ons ranging from 4 to 20%, apart from 2-methylpiperazine-deriving PAAs

that never extinguish flame but slow down flame propagation leaving a substantial residue. In vertical flame spread tests, no PAA induces flame extinguishment at add-ons up to 20%, but all PAA-treated fabrics leave significant residues. In cone calorimetry tests, all PAAs increase the time to ignition and decrease the peak of heat release rate and the effective heat of combustion. Most PAAs remarkably reduce the release of CO and CO_2. After the above tests the combustion residues of PAA-treated cotton fabrics present intumescent bubbles. All results indicate that PAAs warrant potential as effective surface-confined intumescent flame retardants.

1. Introduction

Fire accidents constitute a major security threats worldwide. In 2016, as officially reported [1], 2.7 million fire accidents took place in 43 Countries, causing 20.7 thousands casualties. Many fires are accidentally triggered indoor on textiles present as curtains, covers of armchairs and sofas, clothes or linens based on cotton or similar easily flammable cellulosic materials. Not surprisingly, many efforts have been and are still devoted to the development of safe and effective flame retardant (FR). As regards cotton fabrics, phosphorylated compounds, for instance tetrakis (hydroxymethyl) phosphonium salts and N-methylol dialkyl phosphonopropionamides, have been the predominant FR for 50 years [2]. However, most of these products have a recognized environmental impact, due to the release of formaldehyde during manufacturing and service life [2]. Many innovative phosphorus containing FR were subsequently published and thoroughly reviewed [3]. The increasingly restrictive national and international regulations [4,5] are pushing scientists to address the development of new and more environment-friendly non-toxic cotton FR with performances comparable to the conventional ones. To this purpose, many biomolecules [6,7], including polysaccharides, lignin, deoxyribose nucleic acid (DNA) [8], proteins [9], phytic acid [10] and vegetable oils [11] have been considered. Their effectiveness was ascribed to their ability to induce char formation in cotton by releasing carboxylic, phosphoric or sulfuric acids by thermal decomposition.

Linear polyamidoamines (PAAs) are a family of synthetic polymers endowed with exceptional structural versatility, which had been reviewed in several instances [12]. They are prepared by stepwise polyaddition of *prim-* or *sec*-amines to bisacrylamides through environment friendly and easily scalable processes carried out in water at room temperature with neither organic solvents, nor added catalysts, nor by-products. Nearly all conceivable bisacrylamides and *prim-* or *sec*-amines can be employed as monomers introducing different functions as side substituent [13]. In particular, it is possible to assemble in a single PAA chemical functions typical of different components normally present in intumescent FR formulations, as for instance non-flammable gas sources such as carboxyl-, amine- and guanidine groups [14].

PAAs can be designed to be biocompatible. All of them slowly degrade in water at pH ≥ 7 to non-toxic products [15,16]. They are normally cationic, due to the presence of *tert*-amine groups in the main chain. However, PAAs carrying acid pendants are amphoteric [17-20]. The chain structure and side substituents of many PAAs remind those of proteins recently found endowed with flame retardant properties [21]. Moreover, when assessed, the thermogravimetric analyses (TGA) of PAAs showed decomposition onset temperatures > 200 °C [20], comparable with- or even higher than those of some proteins, e.g. whey proteins [22]. The structural features and thermal decomposition pattern of PAAs suggested that they could act as FR. This was borne out in practice.

A different family of hyperbranched polymers containing amide- and amine groups in the chain, named PAMAMs, have been grafted on cotton after silanization with 3-aminopropytriethoxysilane, and subsequently phosphorylated, to impart fire-retardant properties [23]. PAMAMs are different from PAAs since, besides being hyperbranched instead of linear, their chain architecture is different. To our present knowledge, PAAs have never been considered as FR for cotton or other cellulosic materials.

The aim of this paper is to report on the performance of a library of PAAs, most of which hitherto undescribed, as cotton surface-confined FR, establishing in the meantime correlations between activity and structural features.

4. Experimental Section

Materials: Glycine (GLY, 98%), ethylenediamine-N,N′-disuccinic acid trisodium salt (EDS, 35% aqueous solution), 2-methylpiperazine (MEP, 95%) 4-aminobutylguanidine (AGM, 97%), L-arginine (ARG, 98%), N,N'-methylenebis(acrylamide) (M, 99%), LiOH monohydrate (98%), NaCl, 0.1 M NaOH standard solution, HCl (37% aqueous solution) and D_2O (99.9%) were purchased from Sigma-Aldrich and used as received. Aqueous solutions were prepared using 18.2 MQ deionized water obtained with a Q20 Millipore system. 2,2-Bis(acrylamido)acetic acid (B, 98%) was synthesized as previously described [17]. Cotton fabric having an area density of 200 g m^{-2} was purchased from Fratelli Ballesio S.r.l. (Torino, Italy).

Synthesis of PAAs: *B-EDS.* B (19.80 g; 0.10 mmol) and LiOH monohydrate (4.20 g; 0.10 mmol) were dissolved in water (35 mL). GLY (7.50 g; 0.10 mmol) and LiOH monohydrate (4.20 g; 0.10 mmol) were added to the solution. The reaction mixture was gently magnetically stirred for 5 days at room temperature in the dark under nitrogen. It was then diluted to 300 mL with water, the pH adjusted to 4.5 with 37% hydrochloric acid and ultra-filtered through a membrane with nominal molecular weight cut-off 5000. The product was finally retrieved by freeze-drying the retained portion.

All other PAAs were prepared as described for B-EDS, using the amounts of reagents reported in Supporting Information (Table S1). The average molecular weight values were determined by Size Exclusion Chromatography (SEC) (Table S1).

All PAAs were characterized by nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR, Figure S1 and S2) and infrared spectroscopy (Figure S3).

Characterizations: The thermal and thermo-oxidative stability of PAAs and PAA-impregnated fabrics was evaluated by thermogravimetric analysis (TGA) in nitrogen and air, respectively, from 30 to 800 °C with a heating rate of 10 °C min^{-1}. A Mettler-Toledo (Milano, Italy) thermogravimetric balance, TGA/DSC 2 Star$^®$ System, was used, placing samples (5 mg) in open alumina pans, in an inert or oxidative atmosphere (50 mL min^{-1} gas flow).

The surface morphology of untreated and impregnated cotton and combustion residues was studied using a LEO-1450VP Scanning Electron Microscope (SEM) (5 kV beam voltage, 15 mm working distance). Fabric pieces or residues (5 x 5 mm^2) were fixed to conductive adhesive tapes and gold-metalized.

Treatment of Cotton Fabrics with PAAs: Stripes of cotton fabrics of the appropriate dimensions were dried for 2 min at 100 °C and weighed. A 5 wt.-% PAA aqueous solution was uniformly drop-wise distributed on the specimens. After deposition, samples were dried 5 min at 100 °C. The total dry solid add-on (wt.-%) was determined by weighing each sample before (W_i) and after impregnation with the PAA solution and drying (W_f), using an analytical balance (±10^{-4} g accuracy). The add-on was calculated according to Equation 1:

$$\text{Add-on} = [(W_f - W_i)/ W_i] \times 100 \qquad (1)$$

Combustion Tests of PAA and PAA-Treated Cotton Fabrics: PAA ignitability was assessed applying a methane flame (20 mm length) for 10 s directly to the freeze-dried polymer powder (~500 mg) placed on a ceramic backing pad, as already performed for other FR such as DNA and caseins [21]. All specimens were conditioned to constant weight at 27 ± 1 °C at 70 % relative humidity. The experiments were performed in duplicate.

The flame retardant properties of PAA-treated cotton fabrics were tested by studying their reaction to a direct flame application (i.e., horizontal and vertical flame spread tests) and to an irradiative heat flux, that is, cone calorimetry tests.

Combustion flame spread tests were carried out in horizontal and vertical configuration on rectangular 25 x 50 mm^2 (horizontal) and 50 x 100 mm^2 (vertical) specimens positioned in a metallic frame. Those for horizontal spread tests were tilted by 45° along the longer y-axis. In all tests a methane flame (20 mm length) was applied on the short side of the specimen for 3 s. All tests were repeated in triplicate. The combustion time and rate, the char length and weight of the final

residue were evaluated. Combustion time (s) and rate (mm s^{-1}) in the presence of flame, combustion time (s) and rate in the presence of afterglow (mm s^{-1}), total combustion time (s) and rate (mm s^{-1}), and final residue (%) were assessed and compared with those of untreated cotton.
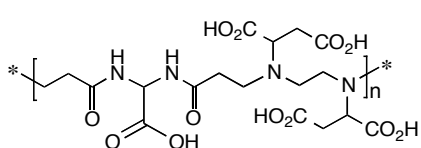
The resistance to an irradiative heat flux of square fabric samples (100 x 100 mm^2) was investigated using oxygen consuming cone calorimeter (Fire Testing Technology). Measurements were carried out under 35 kW m^{-2} irradiative heat flux in horizontal configuration, following the procedure described elsewhere[24] and derived from ISO 5660 [25]. Parameters such as the time to ignition (TTI, s), effective heat of combustion of volatiles (EHC, kW kg^{-1}), total heat release (THR, kW m^{-2}) and peak of heat release rate (PHRR, kW m^{-2}) were measured. Average carbon monoxide [CO] and carbon dioxide [CO$_2$] yields (both expressed in kg kg^{-1}) and [CO] and [CO$_2$] release on time (both expressed in g s^{-1}), and residual mass fraction (RMF, wt.-%) were assessed as well. In order to establish an efficiency ranking of the PAAs under study, the fire performance index (FPI), that is, the TTI to PHRR ratio, was calculated: the higher the FPI, the more efficient was the flame retardant system [26]. Prior to combustion tests, all specimens were conditioned to constant weight at 23 ± 1 °C for 48 h at 50 % relative humidity in a climatic chamber. The experiments were performed in triplicate for each sample calculating the experimental error.
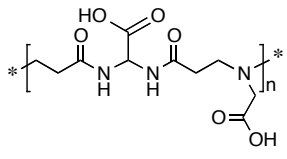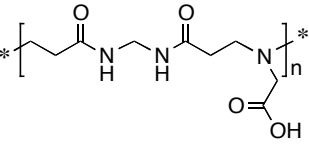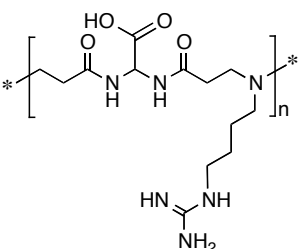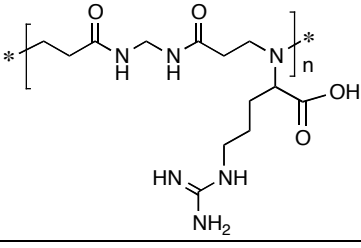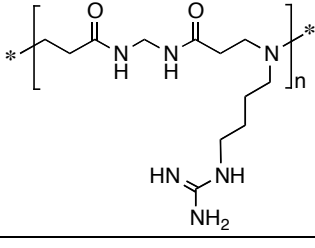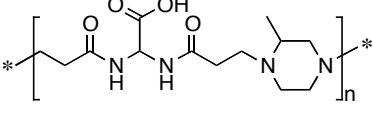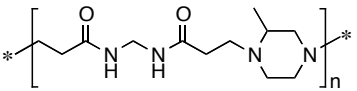
2. Results and Discussion

2.1. PAA Synthesis and Acid-Base Properties Determination

The repeat units of the PAAs considered in this work are shown in Table 1.

Table 1. PAAs investigated as flame retardants for cotton fabrics.

Polymer	Structure of the repeating unit [r.u.]	pK$_a$ values [β]	COOH/r.u. [wt.-%]	HCl/ r.u. [wt.-%]	IP [b)]
B-EDS[a)]		pK$_{a1}$, pK$_{a2}$< 1 pK$_{a3}$ 2.5 pK$_{a4}$ 3.7 pK$_{a5}$ 4.6 pK$_{a6}$ 6.1 pK$_{a7}$ 10.5	45.9	-	< 2

B-GLY[a)]		$pK_{a1} <$ 1 (1.0) pK_{a2} 2.5 (1.5) pK_{a3} 8.3	32.9	-	< 2
M-GLY[a)]		pK_{a1} 1.9 (0.5) pK_{a2} 7.7 (1.5)	19.6	-	4.8
B-AGM [27]		pK_{a1} 3.1 (1.2) pK_{a2} 7.4 pK_{a3} 11.3	13.7	11.1	10.0
M-ARG [18,19]		pK_{a1} 2.2 (0.6) pK_{a2} 6.4 (1.1) $pK_{a3} >$ 10	13.7	9.0	9.7
M-AGM[a)]		pK_{a1} 7.1 (1.6) $pK_{a2} >$ 10	-	32.0	-
B-MEP [27]		$pK_{a1} <$ 2 (1.0) pK_{a2} 3.3 pK_{a3} 7.7	15.1	0.9	5.5
M-MEP[a)]		pK_{a1} 3.0 (1.1) $pK_{a2} =$ 7.1	-	15.0	-

[a)] New substance; [b)]Isoelectric Point.

All of them were planned to contain in the main chain the CO-NH-CH-NH-CO sequence reminiscent of the peptide bond. In addition, all PAAs except M-MEP contained functional side substituents found in proteins, namely carboxyl and/or guanidine groups. They were all prepared in a single step by stepwise polyaddition of amines with bisacrylamides (Scheme S1) under the conditions mentioned in Introduction [12].

Their number-average molecular weights, $\overline{M}_n$, (Table S1) ranged between 4.5 and 8.5 KDa, with polydispersity (*PD*) ~ 1.5. Besides structures, Table 1 shows the protonation constants (*pKa*) of all PAAs tested, the isoelectric points (*IP*) of the amphoteric ones, the average weight percentages of carboxyl groups and hydrochloric acid, if any, present at the pH of the impregnating solutions, that is 4.5. The protonation constants were determined from potentiometric titrations using the generalized Henderson-Hasselbach Equation (2):

$$pH = pK_a - \beta\ log(1-\alpha)/\alpha \qquad (2)$$

where K_a is the weak acid dissociation constant being pH-determining in the buffer titration zone considered; *α* is the acid dissociation degree; *β* is the Katchalsky and Spitnik parameter [28] accounting for possible interactions between ionizable groups on repeat units being spatially or topologically adjacent. The speciation diagrams, obtained from the *pKa* values reported in Table 1, are shown in Figure S4.

2.2. PAA Thermal Stability

Figure 1 compiles the TG thermograms of all PAAs in both nitrogen and air between 30- and 800 ˚C. Thermal data, including onset temperature at 10% weight loss, $T_{onset10\%}$, temperature at maximum weight loss rate, T_{max}, and residual weight (measured at 750 ˚C and expressed as a percentage of the original weight) are reported in Table S2 and S3. B-EDS, B-GLY, M-GLY and B-AGM, M-ARG, M-AGM exhibited multimodal weight-loss curves in both nitrogen and air. This behavior suggested complex thermal decomposition mechanisms, in line with their multifunctional nature. For these PAAs, the degradation onset ranged from 185 to 221 ˚C in nitrogen and from 118 to 228 ˚C in air. In both cases it occurred at significantly lower temperatures compared with untreated cotton, which started decomposing around 320 ˚C both in nitrogen and air (see Figure 4). For all PAAs, the T_{max} of the main decomposition step in nitrogen ranged from 229 to 312 ˚C, whereas in air they exhibited several different T_{max} values, the most important two occurring

between 229 and 267 °C and between 435 and 630 °C (T_{max1} and T_{max2}). The TG traces in air compared with those in nitrogen showed a significant lower weight loss in the temperature ranges 300-570 °C for B-EDS, B-GLY, M-GLY; 350-550 °C for B-AGM, M-ARG, M-AGM and 350-500 °C for B-MEP, M-MEP.

Noticeably, all PAAs heated in air up to 450 °C in the TGA crucible, formed porous "muffin-like" carbonaceous structures (Figure 1b) testifying their tendency to intumesce. All PAAs except B-MEP, M-MEP left substantial char residues in nitrogen: 24-29% (B-EDS, B-GLY, M-GLY); 16-23% (B-AGM, M-ARG, M-AGM) and still significant residues in air: 7-13% (B-EDS, B-GLY, M-GLY); 2-6% (B-AGM, M-ARG, M-AGM). B-MEP, M-MEP behaved differently. They both underwent a substantial weight-loss (~ 60%) in a small temperature interval (around 355 °C and 360 °C, respectively). Moreover, their residual masses in nitrogen (7%) and air (2%) were smaller than those of all other PAAs (Table S2 and S3). This was attributed to the intumescent behavior of PAAs, which occurs in air, but not in nitrogen, where PAAs thermally mostly degrade to volatile products.

2.3. Ignitability tests

The ignitability of PAAs was assessed by direct flame impingement for 10 s on neat freeze-dried powders (snapshots reported in Figure 2).
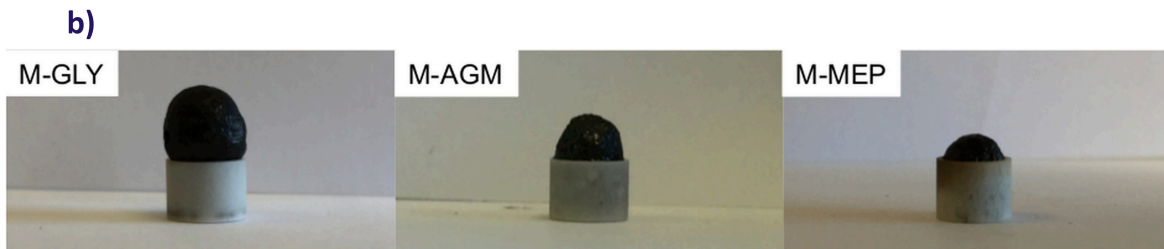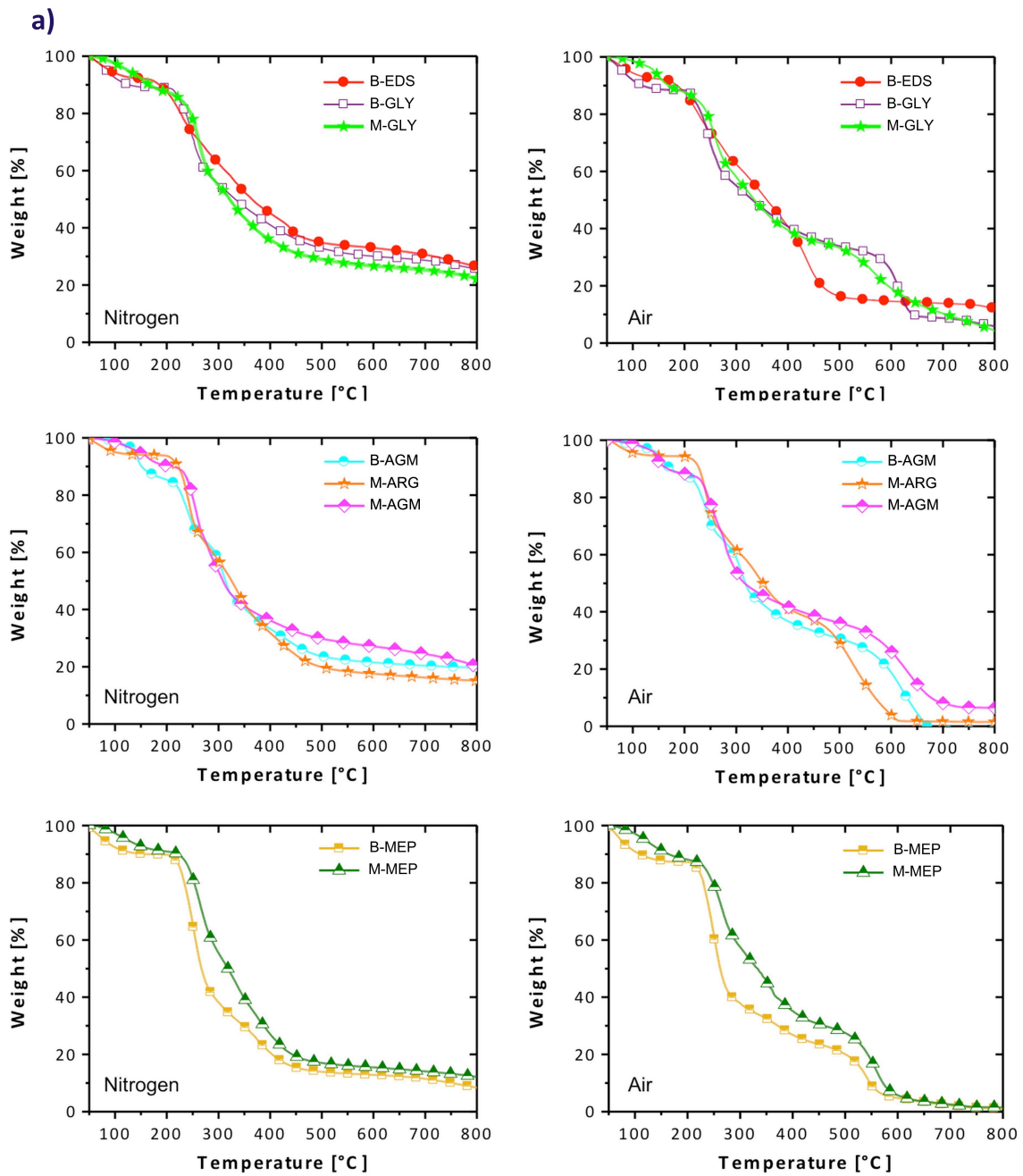
Figure 1. TGA of PAAs: a) TG curves in nitrogen and air; b) aspect of M-GLY, M-AGM and M-MEP sample residues in a TGA crucible after heating up to 450 °C in air.

The results showed three distinct behaviors. B-EDS (Figure 2a), B-GLY, M-GLY did not ignite upon flame application: their surfaces underwent pyrolysis becoming dark-brown and generating

porous carbonaceous crusts sheltering the underlying powders that remained white and integer, with minimal (<5%) weight loss. Also B-AGM, M-ARG (Figure 2b), M-AGM did not ignite but partially volatilized leaving off-white residues accounting for 45% of the original weight. B-MEP (Figure 2c) and M-MEP almost completely burnt and volatilized (>90% mass loss) forming bubbles.
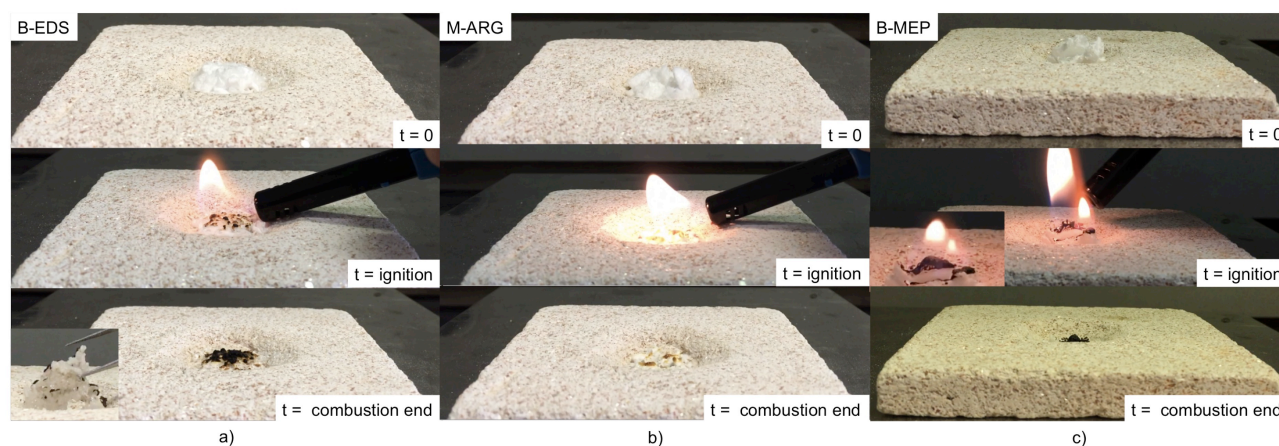

Figure 2. Snapshots of the flame tests for B-EDS, M-ARG and B-MEP.

B-EDS, B-GLY, M-GLY were characterized by the presence of one or more carboxyl groups in the amine sub-unit. B-MEP, M-MEP were both ignitable notwithstanding the carboxyl group present on the bisacrylamide sub-unit of the former. These results suggested that the presence of carboxyl groups in the amine sub-units was the main factor imparting ignition resistance. It is well known that β-aminoethylamides, such as PAAs, on heating decompose to acrylamides and amines by retro-Michael reaction [29]. Based on this consideration, the flammability of B-MEP, M-MEP and the ignition-resistance of B-EDS, B-GLY, M-GLY were explained by the fact that the former two released the volatile (b.p. 155 °C) and flammable 2-methylpiperazine, whereas the remaining three released non-volatile aminoacids that, in addition, were liable to give-off carbon dioxide.

Also guanidine pendants played a major role in inhibiting ignition, as demonstrated by the results of B-AGM, M-ARG, M-AGM, although at the expense of a considerable weight loss. It was speculated that the first step produced either agmatine or arginine, followed by decomposition of the guanidine group to ammonia [30-32], as reported in the case of L-arginine hydrochloride [33].

2.4. Treatment of cotton fabrics

Combustion tests were carried out on cotton fabrics impregnated with PAA aqueous solutions at pH 4.5 and then dried. This pH value was adopted since it corresponded to maximum hydrolytic stability (Figure S4), since PAA degradability in aqueous media at pH >7 was attributed to the presence of nucleophilic *tert*-amine *β* to amide functions [34]. The presence on fabrics of PAA coating was ascertained by FTIR-ATR spectroscopy (Figure S5). The surface morphology of PAA-treated cotton fabrics was assessed by SEM observation. Representative examples of cotton/PAA SEM micrographs with magnification 2500X are shown in Figure 3.
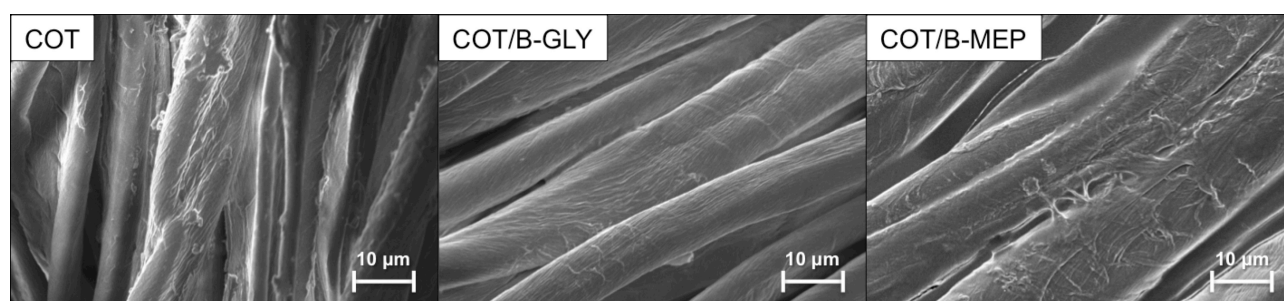

Figure 3. SEM micrographs of untreated cotton and PAA-treated cotton fabrics with add-on values 4% (COT/B-GLY) and 19% (COT/B-MEP). (2500X).

Figure S6 and S7 show the morphologies of cotton fabrics treated with all PAAs considered with magnification 2500X and 1000X. The morphology of PAA-treated cotton showed clear add-on dependence.

Fibers of both untreated and PAA-treated cotton maintained the original spiralization of cellulose fibrils. The fiber surface was generally flat and smooth, but with a significant level of inhomogeneities related to its natural origin. With 3.5-4% add-on of B-EDS, B-GLY, M-GLY the fiber surface was smoother than in untreated cotton and coated by a continuous thin film preserving fiber individuality. Instead, with 19.0% add-on coatings of B-AGM, M-ARG, M-AGM and B-MEP, M-MEP filled the interstitial space and most fibers lost their individuality.

2.5. Thermal Stability of PAA-Treated Cotton Fabrics

Figure 4 reports the TG thermograms of all PAA-treated fabrics in the range 30-800 ˚C in both nitrogen and air. The add-on values of B-EDS, B-GLY, M-GLY and B-AGM, M-ARG, M-AGM classes were the minimal inducing extinguishment in horizontal flame spread tests, that is, 4% for B-EDS, B-GLY, M-GLY and 19% for B-AGM, M-ARG, M-AGM. Also the add-ons of B-MEP, M-MEP, unable to extinguish flame, were 19%. Thermal data are summarized in Table S4 and S5. Overall, all PAAs sensitized cotton thermal decomposition reducing $T_{onset10\%}$, in both nitrogen and air, but with qualifications. For instance, B-EDS, B-GLY, M-GLY reduced cotton $T_{onset10\%}$ in nitrogen (323 °C) to 287-306 °C, less than B-AGM, M-ARG, M-AGM (266-276 °C) and B-MEP, M-MEP (255-260 °C), in line with their much lower add-on values. The temperatures of maximum weight loss rate, T_{max}, of PAA-treated fabrics were in all cases lower than that of cotton (Figure 4 and Table S4). As for plain PAAs, the TG traces in air of PAA-treated cotton fabrics showed, compared with those in nitrogen, a significant lower weight loss at temperature higher than 350 °C, although less evident and in a narrower temperature interval for B-EDS, B-GLY, M-GLY, possibly due to their much lower add-on.

The residues left at 350-370 °C were thermally stable up to 800 °C in nitrogen, but underwent oxidative decomposition and mostly volatilized in air. In all cases the residues at 800 °C in both nitrogen and air, however small, were higher for PAA-treated cotton compared untreated cotton.

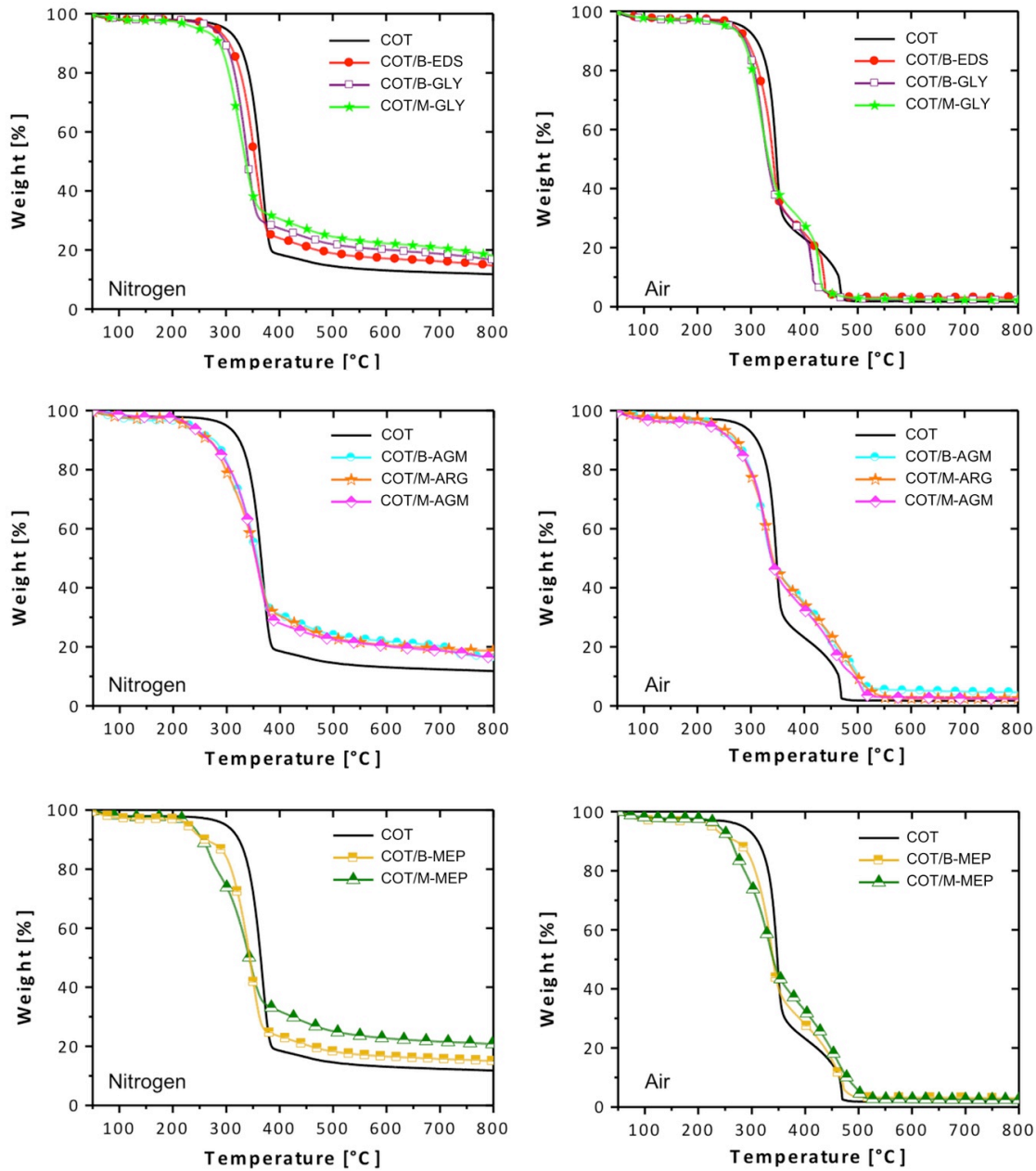**Figure 4.** TG curves of PAA-treated fabrics in nitrogen and air.

2.6. Combustion tests

2.6.1. Horizontal flame spread tests

The combustion behavior of PAA-treated cotton fabrics was first assessed by horizontal flame spread tests on specimens with add-ons in the range 2-30%. The snapshots of combusted PAA-treated cotton fabrics are shown in Figure 5 and the results reported in Table 2.

Figure 5. Snapshots of horizontal flame spread tests for neat cotton and cotton treated with PAAs. a) B-EDS, B-GLY, M-GLY; b) B-AGM, M-ARG, M-AGM and c) B-MEP, M-MEP.

All data proved that the majority of tested PAAs gave fireproofing coatings imparting cotton self-extinguishment within the above add-on interval. Their relative effectiveness was ranked based on both the minimum add-on value needed to reach self-extinguishment, the lowest char length and the highest residue. B-EDS, B-GLY, M-GLY were the best performing ones. These PAAs rapidly stopped cotton combustion at very low add-ons (3.5-4%) after burning very limited areas (Figure 5a) in a shorter time (42-48 vs. 52 s for PAA-treated and untreated fabrics, respectively) under a lower combustion rate (0.3-0-4 vs. 1.0 mm s^{-1}), leaving a very high residue (60-87%). The

importance, in this respect, of carboxyl groups in the amine sub-unit of B-EDS, B-GLY, M-GLY was already discussed in the "ignitability test" paragraph.

The guanidine containing B-AGM, M-ARG, M-AGM slowed down (0.4-0.7 mm s s^{-1}) cotton combustion, but compared with B-EDS, B-GLY, M-GLY needed considerably higher add-ons (19%) to induce extinguishment after burning substantial areas (Figure 5b) and left slightly higher residues (82-92%). In line with the observed ignitability (Figure 5c), B-MEP, M-MEP were unable to extinguish cotton combustion up to 30% add-on. However, compared with untreated cotton, the treated cotton showed higher combustion time (98 and 80 s, respectively, vs. 52 s) and left important char residues (45 and 50%, respectively). As a final observation, the PAA solutions used for impregnation had pH 4.5, adjusted with hydrochloric acid when opportune (see Table 1). The release of hydrochloric acid had been reported as an important element governing flame-retardancy, since it thermally decomposes to chlorine radicals (Cl$^{\bullet}$) acting as radical scavengers blocking formation of volatile flammable products [31]. In the case of PAAs, this effect was apparently overshadowed by more cogent elements, including the volatility of the amine released by the thermally induced retro-Michael reaction.

Table 2. Combustion data of PAA-treated cotton fabrics from horizontal flame spread tests.

Sample	Add-on[a] [%]	Combustion		Char length[b] [mm]	Extinguishment [YES/NO]	Residue [wt.-%]
		time[b] [s]	rate [mm s^{-1}]			
COT	-	52	1.0	-	NO	-
COT/B-EDS	3.5	42[c]	0.4	18	YES	60
COT/B-GLY	3.5	48	0.3	14	YES	87
COT/M-GLY	4.0	48	0.4	18	YES	82
COT/B-AGM	19.0	30	0.7	22	YES	92
COT/M-ARG	19.0	46	0.7	34	YES	81
COT/M-AGM	19.0	31	0.7	23	YES	93
COT/B-MEP	19.0[d]	80	0.5	50	NO	45
COT/M-MEP	19.0[d]	98	0.5	50	NO	50

[a] Minimum add-on imparting self-extinguishment; [b] Experimental error: 2 s for combustion

time, 2 mm for char length; [c] 82 s accounting for afterglow; [d] Self-extinguishment never occurred for add-ons up to 30%.

SEM micrographs of the combustion residues of PAA-treated cotton fabrics showed that the burnt areas of the self-extinguished fabrics maintained the original shape and texture, whereas in the case of non-extinguished fabrics (COT/B-MEP and COT/M-MEP), the residues consisted of partially consumed fibers (Figure 6 and S8). The combustion residues of cotton fabrics treated with B-EDS, B-GLY, M-GLY exhibited dense intumescent bubbles (Figure 6 and S9). The residues of fabrics treated with B-AGM, M-ARG, M-AGM showed only a few bubbles (Figure 6 and S10), probably due to extensive volatilization of the PAA coating. The residues of fabrics treated with B-MEP, M-MEP were nearly devoid of bubbles. All the above results were in line with those of ignitability tests previously reported.
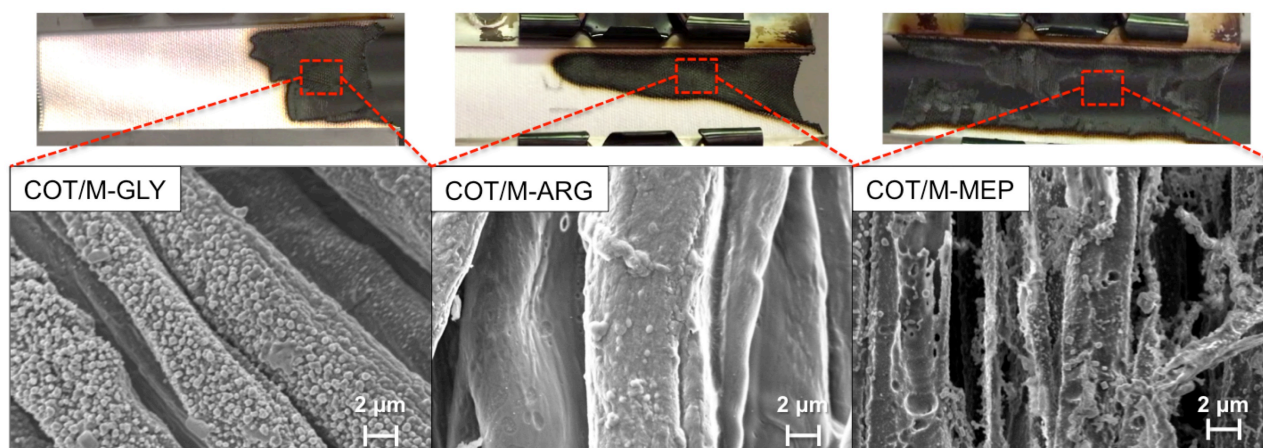

Figure 6. SEM micrographs of the combustion residues of representative examples for cotton fabrics treated with PAAs with different structural features from horizontal flame spread tests. (5000X).

2.6.2. Vertical flame spread tests

Vertical flame spread tests were performed with add-ons up to 20%. No extinguishment was observed for any PAA. The results are reported in Table 3.

In addition, snapshots of combusted PAA-treated cotton fabrics are shown in Figure S11.

In all cases, except COT/M-ARG and COT/M-AGM, a residual afterglow was observed consuming part of the residue. The total combustion time, given by the sum of the combustion time in the

presence of flame and the combustion time in the presence of afterglow, was determined. As regards the former, those of treated cotton specimens were of the same order of magnitude as that of cotton, only slightly higher for COT/B-EDS, COT/B-GLY, COT/M-GLY and COT/B-AGM, COT/M-ARG, COT/M-AGM. Conversely, the afterglow time was generally higher for the treated cotton than for untreated cotton, with the exception of COT/M-ARG and COT/M-AGM for which, in the absence of afterglow, the total combustion time was much lower. In the case of B-AGM, the afterglow consisted of a few scattered points that slowly consumed a minor part of the combustion residue of the in the presence of flame. The result was that its total combustion time was particularly high, but the final residue was of not much lower than of those of COT/M-ARG and COT/M-AGM.

Table 3. Combustion data of PAA-treated cotton fabrics from vertical flame spread tests.

Sample	Add-on [%]	Combustion in the presence of flame		Combustion in the presence of afterglow		Total combustion		Residue[b] [wt.-%]
		time[a] [s]	rate [mm s⁻¹]	time[a] [s]	rate [mm s⁻¹]	time[a] [s]	rate [mm s⁻¹]	
COT	-	18	5.6	27	3.7	45	2.2	0
COT/B-EDS	6.1	16	6.2	80	1.3	95	1.1	7
COT/B-GLY	5.8	24	4.2	116	0.9	140	0.7	7
COT/M-GLY	6.2	17	5.9	56	1.8	73	1.4	12
COT/B-AGM	19.2	24	4.2	95[c]	1.1	119	0.8	16
COT/M-ARG	19.5	20	5.0	0	0	20	5.0	25
COT/M-AGM	19.0	22	4.5	0	0	22	4.5	20
COT/B-MEP	20.0	17	5.9	69	1.5	86	1.2	9
COT/M-MEP	19.7	17	5.9	162	0.6	179	0.6	9

[a] Experimental error: 1 s for combustion and afterglow times; [b] Experimental error: 1.0% for residue; [c] Few points of incandescence that very slowly consumed the residue.

SEM micrographs of the combustion residues of some PAA treated cotton fabrics (Figure 7) showed that in the case of samples subjected to a widespread afterglow (COT/B-GLY and COT/M-MEP) the residue consisted of fibers partially consumed by flame exposure, but still oriented according to the original fabric texture.

On the other hand, for COT/M-ARG (where this phenomenon was not present and the flame glided on cotton surface) the fibers were almost integer and the original texture was preserved.
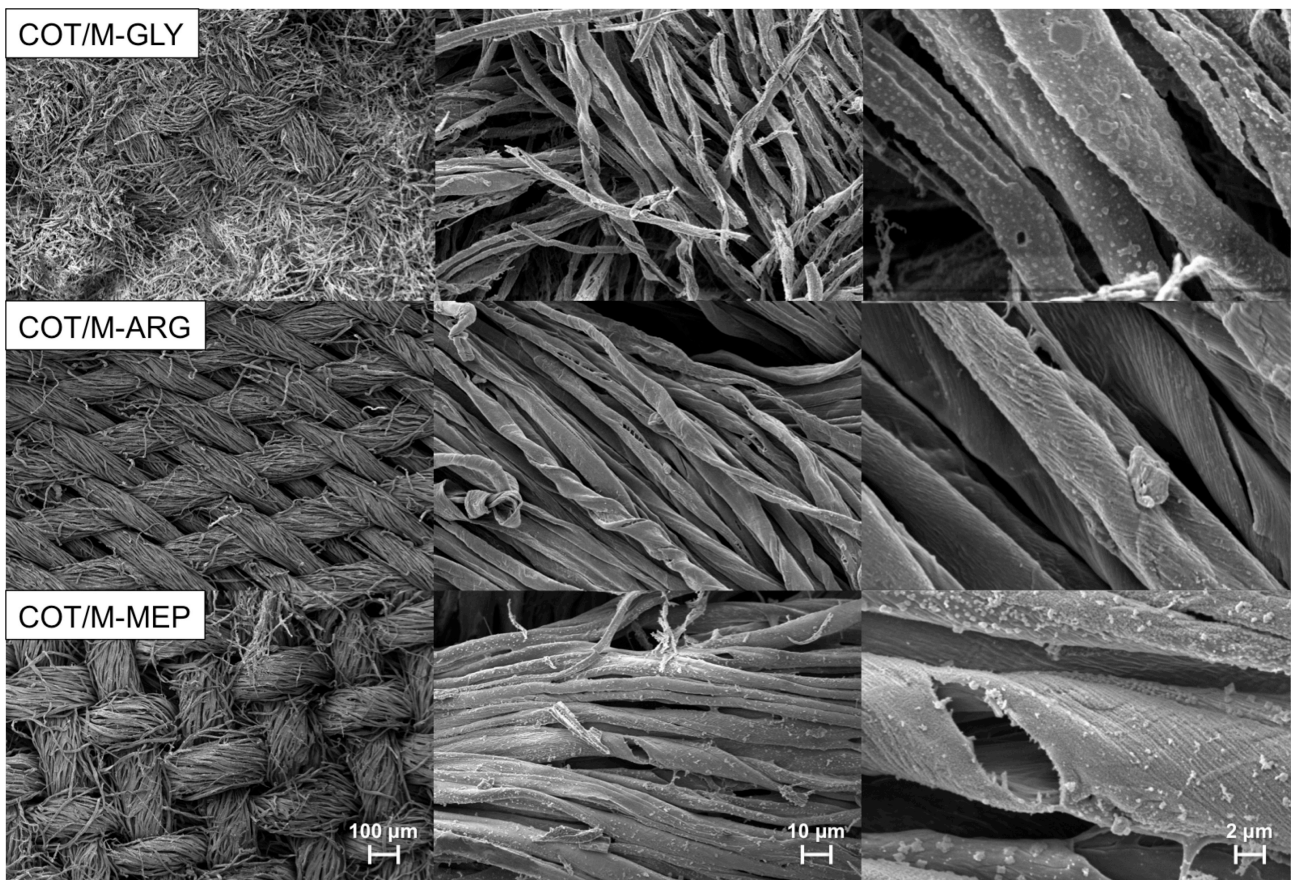

Figure 7. SEM micrographs of the combustion residues of representative examples for cotton fabrics treated with PAAs with different structural features from vertical flame spread tests. (100X, 1000X and 5000X).

2.6.3. Cone calorimetry tests

Cone calorimetry tests were performed since they are apt to simulate a realistic fire scenario [35]. During cone calorimetry tests the samples are exposed, rather than to a small flame as in flame spread tests, to a 35 kW m^{-2} heat flux as normally found in developing fires. As a consequence of the high temperature reached, the sample starts degrading and releasing combustible volatile gases. After a certain amount of time, such gases lead to the ignition of the sample and its subsequent flaming combustion.

The potential of PAAs as surface confined FR of cotton fabrics was studied by exposing PAA treated fabrics to a heat flux of 35 kW m^{-2} capable of bringing the sample surface to approximately 520 °C [35].

Figure 8 compiles the heat release rate (HRR) curves of control and treated fabrics. Combustion parameters such as time to ignition (TTI), peak of heat release (PHRR), effective heat of combustion of volatiles (EHC) and total heat release (THR) are reported in Table 4.

All PAAs changed the shape of cotton HRR curves in a fashion resembling thermally thick charring samples [35]. They all increased cotton resistance to the adopted heat flux, by increasing TTI while significantly decreasing PHRR and EHC. As regards PHRR, some qualifications existed.
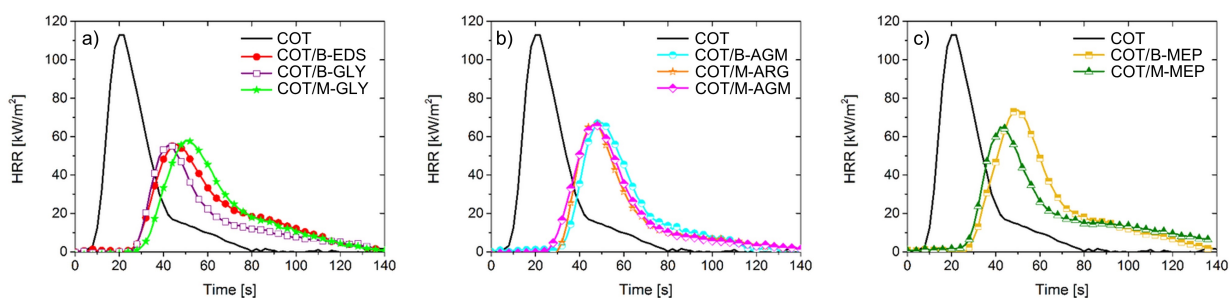

Figure 8. Heat release rate curves of PAAs. (a) B-EDS, B-GLY, M-GLY. (b) B-AGM, M-ARG, M-AGM. (c) B-MEP, M-MEP.

B-EDS, B-GLY, M-GLY, in spite of being tested at the lowest add-ons ($\leq$ 5% vs. 19% for all remaining PAAs), showed the highest PHRR reductions (> 45%), followed by B-AGM, M-ARG, M-AGM (> 38%) and B-MEP, M-MEP (> 29%) in line with the horizontal flame spread tests. The reduction of effective heat of combustion of volatiles (EHC), which describes the heat available per unit of mass loss [35], following PAA treatment was remarkable (38-60%). This result suggested that the amount of combustible volatiles, hence the total fuel support of the flame, was drastically reduced as PAAs formed a coating on cotton fibers acting as protective shield inhibiting heat, mass and oxygen transfer between atmosphere and fabric. This was in agreement with the morphologies of treated fabrics observed by SEM (Figure 3, S6 and S7). No significant differences in THR were found between untreated and PAA-treated cotton fabrics. In fact, the residual mass fraction (RMF) left by the latter was very low.

Table 4. Combustion data of PAA-treated fabrics from cone calorimetry.

Sample	TTI[a] [s]	PHRR[b] [kWm^{-2}]	Δ PHRR [%]	FPI[c] [sm^2 kW^{-1}]	EHC[d] [MJkg^{-1}]	Δ EHC [%]	THR[e] [MJm^{-2}]	RMF[f] [%]
COT	12±4	116±6	-	0.10±0.05	27.5±1.4	-	2.2±0.1	-
COT/B-EDS	19±4	58±3	-50	0.32±0.13	14.0±0.7	-49	2.3±0.1	2.5±0.5
COT/B-GLY	19±4	56±3	-52	0.34±0.13	11.3±0.1	-59	1.9±0.1	3.5±0.5
COT/B-GLY	22±4	64±3	-45	0.34±0.12	14.2±0.7	-48	2.2±0.1	1.5±0.5
COT/B-AGM	22±4	69±4	-40	0.32±0.11	11.6±0.6	-58	2.1±0.1	1.5±0.5
COT/M-ARG	23±4	69±3	-40	0.33±0.12	11.0±0.6	-60	2.0±0.1	5.5±0.5
COT/M-AGM	22±4	72±4	-38	0.30±0.12	11.6±0.6	-58	2.1±0.1	6.0±0.5
COT/B-MEP	22±4	82±4	-29	0.27±0.11	17.0±0.8	-38	2.7±0.1	2.0±0.5
COT/M-MEP	19±4	75±4	-35	0.25±0.11	13.8±0.7	-50	2.4±0.1	3.0±0.5

[a]Time To Ignition. [b]Peak of Heat Release Rate. [c]Fire Performance Index. [d]Effective Heat of Combustion. [e]Total Heat Release. [f]Residual Mass Fraction.

The PAAs were also ranked using the fire performance index (FPI), that is, the TTI to PHRR ratio (Table 4). The higher the FPI, the more efficient is the flame retardant system used [26].

In all cases, the PAA-treated fabrics showed higher FPI values compared with untreated cotton. In line with the results of flame spread tests, B-MEP, M-MEP were the least efficient ones. No significant differences were observed among all other PAAs, provided the different add-ons adopted were not considered.

Figure 9 shows the [CO] and [CO$_2$] release curves of untreated and treated cotton on time and Table 5 lists the yields of both gases.

As already reported [36], the [CO] release curve of cotton consisted of two steps centered at 26 and 66 s, the highest yield occurring at the latter time, whereas that [CO$_2$] showed an asymmetric single peak with maximum centered at 36 s. Treatment with B-EDS, B-GLY, M-GLY caused a remarkable reduction of both [CO] and [CO$_2$] yields (Figure 9a and 9b). In particular, in the [CO] curve the first peak was shifted to > 40 s (42-50 s), whereas the second peak remained around 70 s, but showed a significant area reduction compared with untreated cotton.
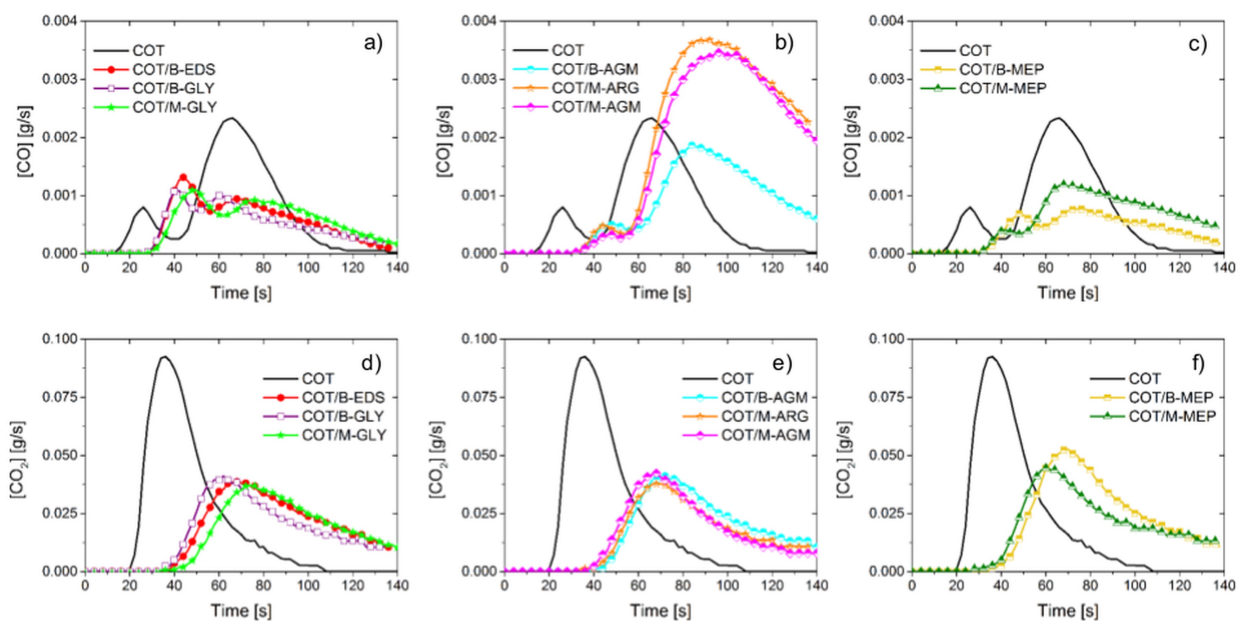
Figure 9. [CO] and [CO$_2$] curves of PAAs. (a and d) B-EDS, B-GLY, M-GLY. (b and e) B-AGM, M-ARG, M-AGM. (c and f) B-MEP, M-MEP.

In the [CO$_2$] release curve the maximum value was shifted, compared with cotton, from 36 s to 68-74 s. In both cases, the area was significantly reduced (28-42% and 26-31% for [CO] and [CO$_2$] yields, Table S7). Similar effects, both as regards [CO] and [CO$_2$] curves, were observed for B-MEP, M-MEP (Table 5, and Figure 9c and 9f). The first peak of [CO] shifted from 26 to 42 and 48 s for M-MEP, B-MEP, respectively, whereas the second peak remained around 70 s (68 and 76 s). The [CO$_2$] peak shifted from 36 to 60 and 68 s. The [CO] and [CO$_2$] reductions were significant and comparable with those of B-EDS, B-GLY, M-GLY, especially as regards [CO] (31-47%). The curves of cotton fabrics treated with B-AGM, M-ARG, M-AGM gave [CO] release curves with different patterns where, compared with cotton, the second peaks shifted to 84-96 s (Table 5, and Figure 9b and 9e). Moreover, compared with cotton, the peak area was slightly lower for B-AGM, but much higher for M-ARG and M-AGM. By contrast, the [CO$_2$] yields of cotton treated with B-AGM, M-ARG, M-AGM were the lowest of all tested samples.

Table 5. [CO] and [CO$_2$] yields of PAA-treated fabrics from cone calorimetry.

Sample	[CO] yield [kg kg^{-1}]	Δ [CO] yield [%]	[CO$_2$] yield [kg kg^{-1}]	Δ [CO$_2$] yield [%]
COT	0.0650±0.0003	-	1.90±0.09	-
COT/B-EDS	0.0423±0.0021	-35	1.40±0.07	-26
COT/B-GLY	0.0376±0.0019	-42	1.31±0.06	-31
COT/B-GLY	0.0465±0.0023	-28	1.40±0.07	-26
COT/B-AGM	0.0626±0.0031	-4	1.29±0.06	-32
COT/M-ARG	0.1368±0.0068	+110	1.13±0.06	-40
COT/M-AGM	0.1277±0.0064	+97	1.14±0.06	-40
COT/B-MEP	0.0342±0.0017	-47	1.74±0.09	-8
COT/M-MEP	0.0446±0.0022	-31	1.36±0.07	-28

Analogously to what observed in vertical flame spread tests, SEM observations (Figure 10) showed that the residues of some PAA treated cotton fabrics after cone calorimetry tests consisted of fibers partially consumed by combustion due to the exposure to 35 kW m^{-2} heat flux, but still oriented following the original texture of cotton fabric.
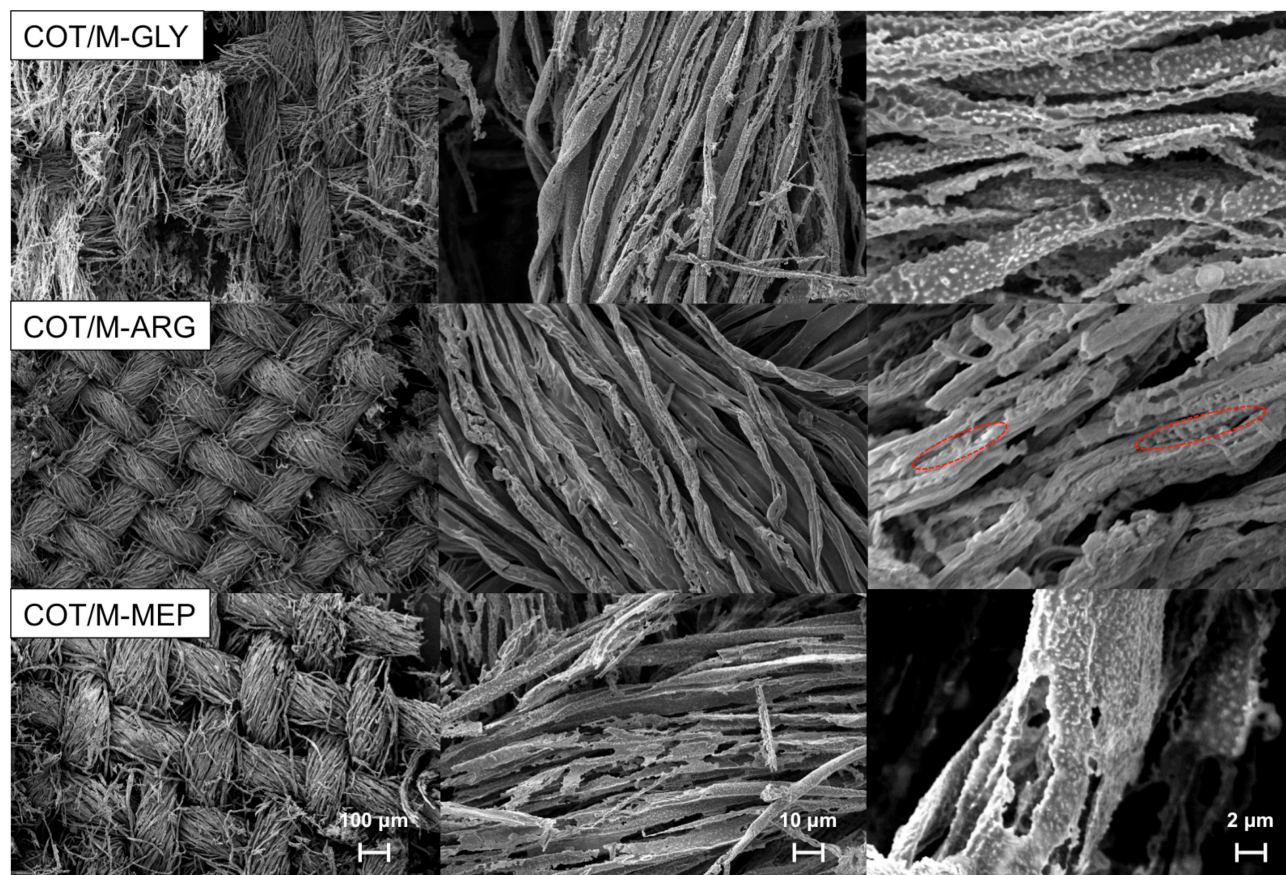
Figure 10. SEM micrographs of the combustion residues of representative examples of cotton fabrics treated with PAAs with different structural features from cone calorimetry tests. (100X, 1000X and 5000X).

Moreover, in COT/B-GLY residue the presence of bubbles due to the intumescence of B-GLY was still visible. In the case of COT/M-ARG, the bubbles were distinguishable only in the internal part of fibers, suggesting that M-ARG was present also in the internal part of the fibers exerting its protective role both on the surface and in the bulk.

Finally, according to what observed in thermogravimetric analyses (Figure 1b), also M-MEP acted as intumescent flame retardant for cotton, since small bubbles were observed after burning on the COT/M-MEP surface.

3. Conclusions

The aim of this paper was to report on a breakthrough work to determine the potential of PAAs as FR. To this purpose, horizontal and vertical flame spread tests and cone calorimetry tests were performed on cotton fabrics treated with dilute aqueous solutions of eight multifunctional linear PAAs previously subjected to direct ignition test. These PAAs contained, except in one case, carboxyl- and/or guanidine side substituents. In addition, the tested PAAs and the related cotton treated fabrics were analyzed by TGA and SEM before and after flame application. The weight and the morphology of the residues after combustion tests were determined. The results of all tests agreed that PAAs containing corboxyl groups on the amine subunits were the most active as FR. Considerable activity was also showed by PAAs carrying guanidine pendants in the amine subunits, whereas those derived from unsubstituted amines were significantly less active irrespectively of the presence of carboxyl pendants on the amide subunit.

Overall, it may be reasonably concluded that PAAs are a class of polymers with remarkable potential as flame retardants for cotton. PAAs are degradable to non toxic products in aqueous solutions within a few months, a feature ruling out environment pollution, but remarkably stable

when dry. The weak point of PAAs, in view of practical applications, is water solubility, hence lack of persistence in home-made laundry. It may be observed, however, that carboxylated PAAs, that is, the most active ones as FR, are completely insoluble in most organic solvents, including those commonly employed in dry-cleaning. Moreover, previous data exist suggesting the feasibility of covalently grafting PAAs on oligosaccharides [37]. It can be reasonably expected that a similar procedure could be adopted for PAA grafting on cotton.

Appendix A. Supplementary data

Supplementary data related to this article were included.

Notes

Acknowledgements

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Graphical abstract

Linear Polyamidoamines as Novel Biocompatible Phosphorus-Free Surface-Confined Intumescent Flame Retardants for Cotton Fabrics

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