Disulfide-containing polyamidoamines with remarkable flame retardant activity for cotton fabrics

Amedea Manfredi[a], Federico Carosio[b], Paolo Ferruti*,[a], Jenny Alongi*,[a], Elisabetta Ranucci*,[a]

[a]Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133 Milano, Italy;

[b]Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Alessandria Campus, viale Teresa Michel 5, 15121 Alessandria, Italy.

*Corresponding Author

E-mail address: paolo.ferruti@unimi.it

Tel.: +39 0250314128

E-mail address: jenny.alongi@unimi.it

Tel.: +39 0250314108

E-mail address: elisabetta.ranucci@unimi.it

Tel.: +39 0250314132

Abstract

Bioinspired polyamidoamines containing disulfide-groups in the main chain (SS-PAAs), prepared by Michael polyaddition of 2,2-bis(acrylamido)acetic acid with *L*-cystine (B-CYSS) and of N,N'-bis(acryloyl-*L*-cystine) with either glycine or 2-methylpiperazine (BACYSS-GLY and BACYSS-MP), were investigated as intumescent surface-confined flame retardants for cotton textiles. The main purpose was to ascertain if the presence of disulfide functions in the repeat units imparted superior flame retardant properties compared with sulfur-deprived polyamidoamines whose efficacy were previously demonstrated. In horizontal flame spread tests, at 18% add-on both BACYSS-GLY and BACYSS-MP inhibited ignition; at 12% add-on BACYSS-GLY extinguished flame, whereas BACYSS-MP burnt completely leaving substantial carbonaceous residues. In vertical flame spread tests, both BACYSS-GLY and BACYSS-MP burnt completely leaving substantial residues up to at least 18% add-on. At 12% add-on B-CYSS inhibited ignition in both horizontal- and vertical flame spread tests. In the latter test, only limited afterglow was observed. Scanning electron microscopy

(SEM), thermogravimetric and cone calorimetric analyses were consistent with these results. In particular, thermogravimetric analyses showed at 750 °C high residues in nitrogen (28-54%) and only moderately lower residues in air (19-48%). In cone calorimetry tests, all tested SS-PAAs increased time to ignition, decreased peak of heat release rate and effective heat of combustion of cotton. All samples remarkably reduced CO and CO_2 yields. SEM micrographs of combustion residues of all SS-PAAs treated cotton fabrics presented diffused intumescent bubbles.

Introduction

In recent works, keratin fibers from tannery industry wastes were reused as both reinforcing- and flame retardant agents (FR) for poly(lactic acid) (PLA)[1] and butadiene-acrylonitrile rubber (NBR).[2] Ground keratin fibers from poultry feathers were used as fillers for polyurethane foams[3] and cotton fabrics for the same purpose.[4] Keratin fibers were also reported to increase polymer thermal stability better than cellulose fibers.[5,6] Among proteins, keratin is particularly rich in cystine-derived disulfide bridges, to which its FR property was attributed.[7] Accordingly, the proven FR effectiveness of non-polymeric disulfides for polypropylene was ascribed to the thermally induced homolytic cleavage of the disulfide group leading to radicals that hinder flame propagation.[8]

Linear polyamidoamines (PAAs) are multifunctional oligomers and polymers prepared by Michael-type polyaddition of bisacrylamides with *prim*-monoamines or bis *sec*-bisamines.[9] Multifunctional amines give crosslinked products.[11,12] In most cases, the polymerization reaction takes place at room temperature in water and neither needs added catalysts, nor involves organic solvents, nor releases by-products. Recently, PAAs have been also found to warrant considerable potential as intumescent, surface-confined cotton FR.[12] Linear PAAs carrying disulfide groups in the main chain, henceforth called SS-PAAs, were previously prepared as potentially bioreducible materials using cystine and cystamine as building blocks.[13,14] In the present work, three SS-PAAs were prepared by polyaddition of 2,2-bis(acrylamido)acetic acid with *L*-cystine (B-CYSS), and N,N'-bis(acryloyl-*L*-cystine) with either glycine (BACYSS-GLY) or 2-methylpiperazine (BACYSS-MP). Their preparation was made possible by the specificity of the Michael addition reaction, which does not affect the disulfide bond, as well as, in the case of B-CYSS, by the large difference of reactivity between the two amine hydrogens of α-amino acids, due to the steric hindrance provided by the presence of two substituents, one of which the bulky carboxylate group, on the carbon atom adjacent to nitrogen.

By analogy with keratin, it was speculated that including disulfide groups in the PAA chains could improve the intrinsic PAA flame retardant properties. The aim of this paper is to report on the

results of an extensive research on the flame retardant properties of B-CYSS, BACYSS-GLY and BACYSS-MP, never studied before in this respect, towards cotton fabrics in order to confirm that disulfide groups improve the flame retardant efficacy of PAAs.

2. Experimental section

2.1. Materials

L-Cystine (CYSS, >98.0%), glycine (GLY, 98%), 2-methylpiperazine (MP, 95%), lithium hydroxide monohydrate (LiOH.H$_2$O, 98%), 0.1 M NaOH standard solution, HCl (37% aqueous solution) and D$_2$O (99.9%) were purchased from Sigma-Aldrich and used as received. Aqueous solutions were prepared using 18.2 MΩ deionized water obtained with a Q20 Millipore system. 2,2-Bis(acrylamido)acetic acid (B, 98%)[15] and N,N'-bis(acryloyl-*L*-cystine) (BACYSS, 98%) were synthesized as previously described.[13] Cotton fabric (COT) having an area density of 200 gm^{-2} was purchased from Fratelli Ballesio Srl (Torino, Italy).

2.2. Characterizations

All SS-PAAs were characterized by ^{1}H nuclear magnetic resonance (NMR). Spectra were obtained in D$_2$O at 25 °C using a Bruker Avance DPX-400 NMR spectrometer operating at 400.13 MHz.

The molecular weights of SS-PAAs were determined by size exclusion chromatography (SEC). SEC traces were obtained with Toso-Haas TSK-gel G4000 PW and TSK-gel G3000 PW columns connected in series, using a Waters model 515 HPLC pump equipped with a Knauer autosampler 3800, a light scattering, a viscometer Viscotek 270 dual detector and a refractive index detector (Waters, Model 2410). The mobile phase was a 0.1 M Tris buffer (pH 8.00 ± 0.05) solution with 0.2 M sodium chloride. Sample concentration: 20 mg mL^{-1}; flow rate: 1 mL min^{-1}; injection volume: 20 µL; loop size: 20 µL; column dimensions: 300 x 7.5 mm^2.

The thermal and thermo-oxidative stability of SS-PAAs and SS-PAA-impregnated fabrics was evaluated by thermogravimetric analysis (TGA) in nitrogen and air, respectively, from 50 to 800 °C with heating rate 10 °C min^{-1}. A Mettler-Toledo thermogravimetric balance, TGA/DSC 2 Star$^®$ System, was used, placing samples (5 mg) in open alumina pans, in either inert or oxidative atmosphere (50 mL min^{-1} gas flow). Prior to analyses, samples were first heated up to 100 °C at 50 °C min^{-1} and maintained at this temperature 3 min.

The surface morphology of untreated and SS-PAA impregnated cotton and combustion residues was characterized using a LEO-1450VP scanning electron microscope (SEM) (5 kV beam voltage, 15 mm working distance) equipped with X-ray probe (INCA Energy Oxford, Cu-Kα X-ray source, k = 1.540562 Å) for performing elemental analysis through energy dispersive X-ray (EDX) and

mapping of the constituents. Fabric pieces or residues (5 x 5 mm^2) were fixed to conductive adhesive tapes and gold-metalized.

SS-PAAs and PAA-treated fabrics were analyzed by attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FT-IR). ATR spectra were recorded at room temperature in the 4000-600 cm^{-1} range (16 scans and 4 cm^{-1} resolution), using a Frontier FT-IR/FIR spectrophotometer (Perkin-Elmer) equipped with a diamond crystal (penetration depth = 1.66 μm).

2.3. Synthesis of SS-PAAs

BACYSS-MP[13] and B-CYSS[14] were prepared essentially as previously described. Briefly:

B-CYSS. 2,2-Bis(acrylamido)acetic acid (B) (1.980 g; 10 mmol) and LiOH monohydrate (0.420 g; 10 mmol) were dissolved in water (4 mL). CYSS (2.430 g; 10 mmol) and LiOH monohydrate (0.840 g; 20 mol) were added to the solution. The reaction mixture was homogenized by gently stirring for 1 h, and then left at 25 °C for six days with occasional stirring. It was then diluted to 50 mL with water, the pH adjusted to 4.5 with 37% HCl. The final product was retrieved by freeze-drying.

^{1}H-NMR (D$_2$O, 400 MHz), δ (ppm): 2.52-2.90 (m, **CH$_2$**CONH); 3.25-3.48 (m, **CH$_2$**S, **CH$_2$**N); 3.90-4.10 (br s, **CH**CH$_2$S); 5.50-5.60 (br s, NH**CH**COOH); 5.70-5.75, 6.10-6.25 (m, **CH=CH$_2$**).

$\overline{M}_n = 1200$ determined by ^{1}H-NMR from the number of terminal groups.

BACYSS-GLY and BACYSS-MP were prepared as described for B-CYSS, using the following amounts of reagents:

BACYSS-GLY: BACYSS (3.48 g, 10 mmol), GLY (0.75 g, 10 mmol), and LiOH monohydrate (1.260 g; 30 mmol).

^{1}H-NMR (D$_2$O, 400 MHz), δ (ppm): 2.75-2.82 (br t, **CH$_2$**CONH); 2.85-3.00, 3.10-3.25 (m, **CH$_2$**S); 3.45-3.51 (br t, **CH$_2$**N); 3.70-3.75 (br s, **CH$_2$**COOH); 4.49-4.52 (br s, **CH**COOH).

SEC data: $\overline{M}_n = 3800, \overline{M}_w = 14000$, PD = 3.7

BACYSS-MP: BACYSS (3.48 g, 10 mmol), MP (1.00 g, 10 mmol), and LiOH monohydrate (0.840 g; 20 mmol).

^{1}H-NMR (D$_2$O, 400 MHz), δ (ppm): 1.24-1.25 (br d, **CH$_3$**); 2.50-2.69 (br m, **CH$_2$**CONH); 2.70-2.85 (br m, N**CH**CH$_3$); 2.90-3.40 (br m, **CH$_2$**S, **CH$_2$**N, N**CH$_2$CH$_2$**N); 4.40-4.45 (br d, **CH**COOH).

SEC data: $\overline{M}_n = 4000, \overline{M}_w = 7000$, PD = 1.8

2.4. Treatment of cotton fabrics with SS-PAAs

Strips of cotton fabrics were dried for 10 min at 100 °C and weighed. 8 wt.-% SS-PAA aqueous solutions were uniformly drop-wise distributed on the specimens. After deposition, samples were dried 10 min at 100 °C. The total dry solid add-on (wt.-%) was determined by weighing each sample before (W_i) and after impregnating with the SS-PAA solution and drying (W_f), using an analytical balance ($\pm 10^{-4}$ g accuracy). The add-on was calculated according to Equation (1):

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

Strips of SS-PAA treated cotton will be identified as COT/SS-PAA code.

2.5. Combustion tests of SS-PAA treated cotton fabrics

SS-PAA ignitability was assessed applying a methane flame (20 mm length) for 10 s directly to the freeze-dried polymer powder (~50 mg) placed on a ceramic spatula. All specimens were conditioned to constant weight at 27±1 °C at 70% relative humidity. The experiments were performed in duplicate.

Combustion flame spread tests were carried out in horizontal and vertical configuration on rectangular 25 x 50 mm^2 and 50 x 100 mm^2 specimens, respectively, 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. 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 residual small fraction (RMF, wt.-%) were assessed and compared with those of untreated cotton.

The resistance to 35 kWm^{-2} 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 in horizontal configuration, following the procedure described elsewhere[16] and derived from ISO 5660.[17] Parameters such as the time to ignition (TTI, s), effective heat of combustion of volatiles (EHC, MJ kg^{-1}), total heat release (THR, MJ 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 SS-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.[18] Prior to combustion tests, all specimens were conditioned to constant weight at 23 ± 1 °C for 48 h at 50%
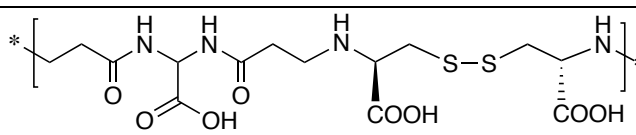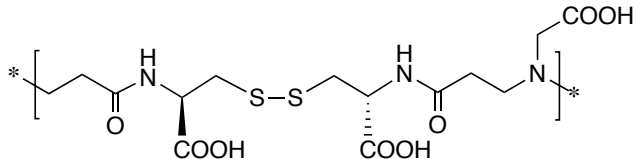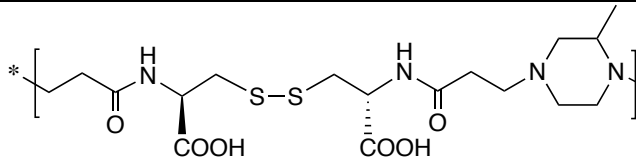
relative humidity in a climatic chamber. The experiments were performed in triplicate for each sample calculating the experimental error.

3. Results and discussion

3.1. Synthesis of SS-PAAs

The repeat units of the SS-PAAs considered in this paper are shown in Table 1. They were prepared in a single step by the polyaddition of 2,2-bis(acrylamido)acetic acid with *L*-cystine (B-CYSS), and of N,N'-bis(acryloyl-*L*-cystine) with either glycine (BACYSS-GLY) or 2-methylpiperazine (BACYSS-MP) according to the usual polyaddition conditions leading to PAAs, that is, in water, at pH 10 and at room temperature. The presence of disulfide bonds did not bias the reaction progress.

Table 1. Disulfide containing PAAs investigated as flame retardants.

SS-PAA	Repeat unit
B-CYSS	
BACYSS-GLY	
BACYSS-MP	

It may be noticed that the SS-PAAs of Table 1 are in some respects structurally similar to proteins. Besides the disulfide groups, they contain side carboxyl groups and, in the chain, the -CO-NH-CH- group reminiscent of the peptide bond.

In a previous study performed with sulfur-deprived PAAs,[12] it was found that the presence of carboxyl groups on the amine-derived subunits dramatically increased FR efficiency, whereas carboxyl groups located on the amide subunits were nearly ineffective. The SS-PAAs considered have two groups potentially active in imparting flame-retardancy, namely disulfide and carboxyl groups. The main aim of this paper was understanding the effect of the presence of disulfide groups, and of their position in the PAA repeat units on the flame retardant properties of PAAs. The structures of SS-PAAs were planned accordingly. In particular (Table 1) BACYSS-MP carries both disulfide and carboxyl groups in the amide subunits; BACYSS-GLY carries both disulfide and

carboxyl groups on the amide subunit and an additional carboxyl group on the amine subunits; B-CYSS carries both disulfide and carboxyl groups in the amine subunits, and additional carboxyl groups on the amide subunits.

3.2. SS-PAA thermal stability

The TG thermograms of B-CYSS, BACYSS-GLY and BACYSS-MP were run both in nitrogen and air in the 50-800 °C temperature range (Figure 1). Relevant thermal data, including onset decomposition temperature (temperature at 10% dry weight loss, $T_{onset10\%}$), temperature at maximum weight loss rate (T_{max}) and residual mass fraction (RMF), measured at 750 °C and expressed as a percentage of the original weight, are reported in Table 2. As previously observed with multifunctional sulfur-deprived PAAs studied as FR for cotton,[12] all SS-PAAs exhibited multimodal weight-loss curves in both nitrogen and air (Figure 1), suggesting complex thermal decomposition mechanisms. For all SS-PAAs, the TG patterns in air were similar to those in nitrogen up to at least 400 °C, with close values of both $T_{onset10\%}$ and T_{max1}. In addition, for all SS-PAAs also the RMF values in nitrogen (54-28%) and air (48-19%) were not much different. In all cases, they were considerably higher than those of sulfur-deprived PAAs (29-7% in nitrogen versus 13-0% in air),[12] supporting the hypothesis that disulfide groups could exert a quenching effect on radical oxidation. Among SS-PAAs, B-CYSS is by far the most thermally stable, both in nitrogen and air. BACYSS-MP is the least stable. Interestingly, in the range 300-450 °C the TG traces of all SS-PAAs showed lower weight loss in air compared with those in nitrogen (Figure 1). This phenomenon was previously observed in sulfur-deprived PAAs and attributed to intumescence. SS-PAAs were heated in air up to 430 °C. Only BACYSS-GLY formed a large amount of swollen porous carbonaceous structures (Figure 1) testifying its tendency to intumesce. This phenomenon was less evident in BACYSS-MP and even less so in B-CYSS, indicating that intumescence was not the main factor responsible for the flame retardancy of SS-PAAs.

Table 2. Thermogravimetric analyses data of SS-PAAs in nitrogen and air.

SS-PAA	$T_{onset10\%}$[a] [°C]	T_{max1}[b] [°C]	T_{max2}[c] [°C]	RMF[d] at 750 °C [wt.-%]
Nitrogen				
B-CYSS	216	200/230/**251**[e]	-	54
BACYSS-GLY	142	137/253/**270**[e]/301	-	35
BACYSS-MP	136	131/152/**270**[e] /277/297	-	28
Air				
B-CYSS	207	200/228/**251**[e]	488	48
BACYSS-GLY	145	137/253/**270**[e]	489	26
BACYSS-MP	144	131/152/260/**280**[e]	548	19

[a] Onset decomposition temperature (temperature at 10% dry weight loss) from dTG curve; [b] first temperature at maximum weight loss rate; [c] first temperature at maximum weight loss rate from dTG curve; [d] Residual Mass Fraction; [e] main decomposition event.
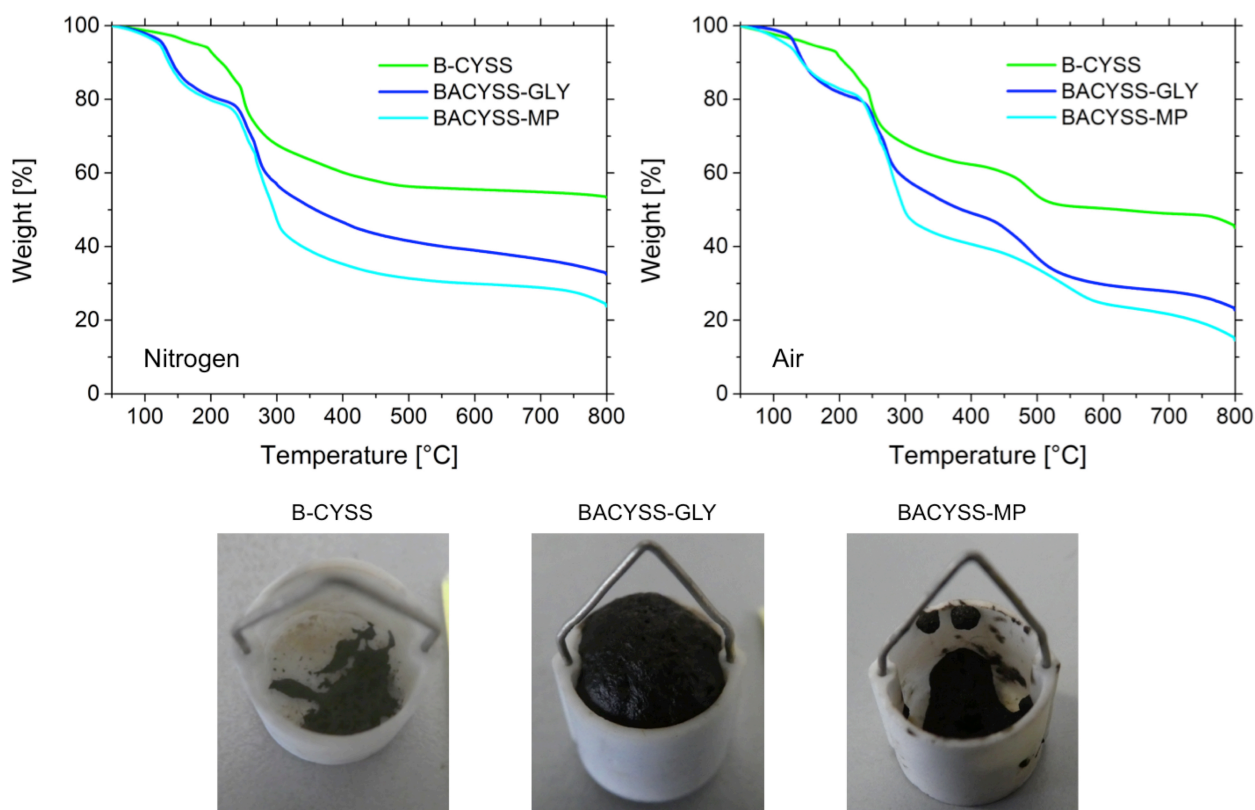

Figure 1. TGA of SS-PAAs: TG traces in nitrogen and air (upper row); pictures of samples heated in air up to 430 °C in alumina pans (lower row).

3.3. Ignitability tests

The ignitability of SS-PAAs was assessed by direct flame impingement for 10 s on powdered samples (Figure 2). None of the samples ignited, but their surfaces darkened. The pyrolized top layers protected the underlying bulk that remained white and underwent minimal weight loss (5-10%). It may be observed that in sulfur-deprived PAAs those whose amine subunits derived from 2-methylpiperazine ignited and burnt with >90% mass loss. This fact was attribute to the release on heating of the volatile and flammable 2-methylpiperazine by retro-Michael reaction. Notwithstanding the amine subunit was the same, BACYSS-MP did not ignite. Since it was unlikely that the release rate of 2-methylpiperazine was much different, it was hypothesized that the thermal decomposition of the disulfide groups gave rise to sulfur radicals quenching flame propagation in the gas phase.
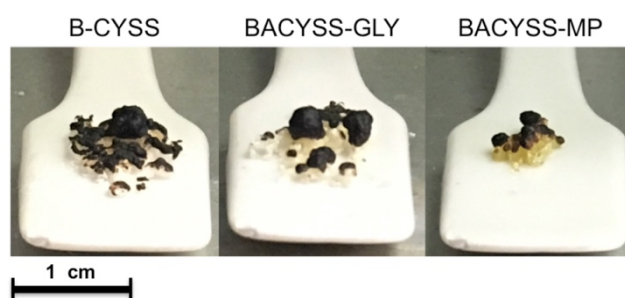

Figure 2. Pictures of SS-PAA residues of ignitability test.

3.4. Characterization of SS-PAA treated cotton fabrics

Cotton fabrics were impregnated with SS-PAA aqueous solutions, previously conditioned at pH 4.5, and dried. The fabrics were first characterized by FT-IR/ATR spectroscopy (Figure 3).

The IR spectra of SS-PAA treated cotton revealed diagnostic bands ascribed to both components, namely 3330 (ν O-H), 2925, 2850 (ν_{as} and ν_{s} CH$_2$), 1370 (δ C-H), 1310 (δ O-H), 1020 (ν C–O), and 894 cm^{-1} (ρ C-H) for cellulose, and 1600 (ν C=O) and ~ 1520 cm^{-1} (δ N-H), less evident in the spectrum of COT/BACYSS-MP, as regards SS-PAAs.
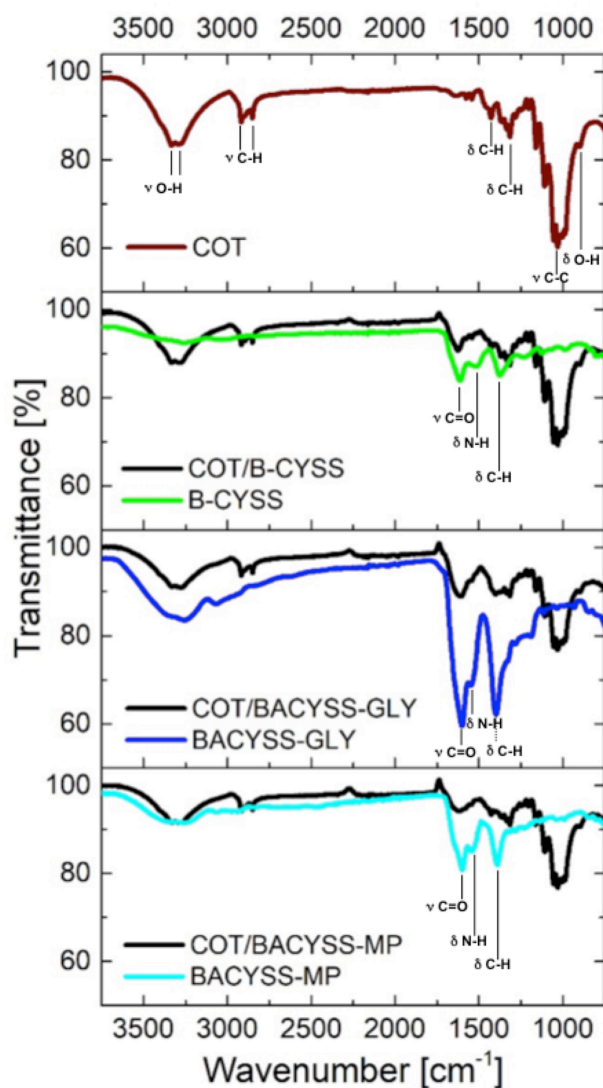
Figure 3. FT-IR/ATR spectra of SS-PAAs and SS-PAA treated cotton.

The SEM micrographs of SS-PAA treated cotton (Figure 4) showed that fibers maintained the natural spiralization and inhomogeneities of cellulose fibrils of cotton, but their surface was smoother and the interstitial spaces were more uniformly filled. EDX analysis demonstrated that the sulfur atoms were evenly distributed on the cotton fabrics and were present on both upper fibers and background (Figure 5). Hence, the SS-PAAs formed on cotton a uniform coating.
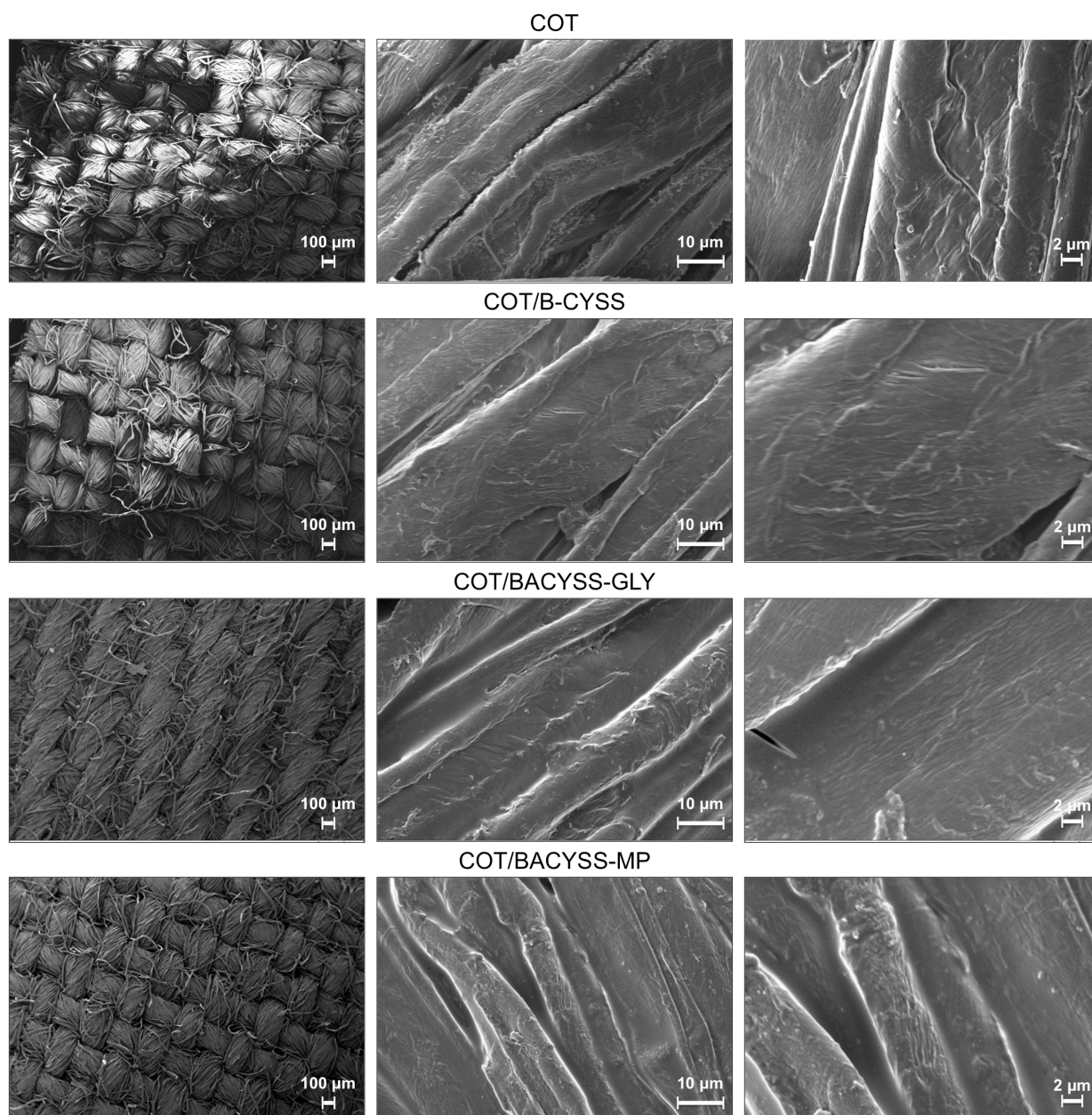
COT

COT/B-CYSS

COT/BACYSS-GLY

COT/BACYSS-MP

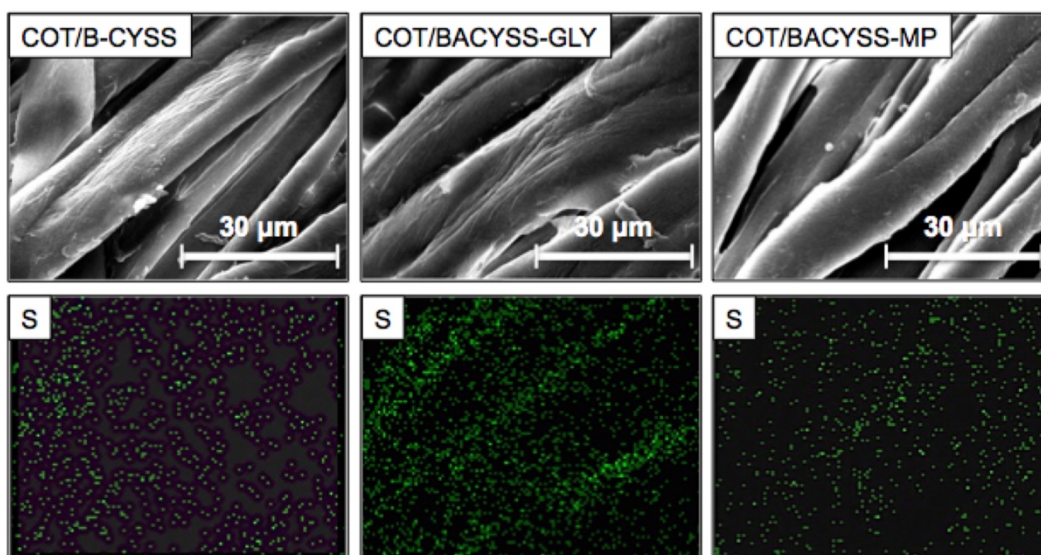**Figure 4.** SEM micrographs of untreated- and SS-PAA treated cotton fabrics.

Figure 5. SEM micrographs with sulfur elemental mapping of SS-PAA treated cotton fabrics.

3.5. Thermal stability of SS-PAA treated cotton

The TG thermograms in both nitrogen and air of SS-PAA treated cotton between 50 °C and 800 °C are reported in Figure 6. The thermal data are summarized in Table 3. It may be noticed that in all cases both $T_{onset10\%}$ and T_{max} of treated cotton were significantly lower than those of cotton, whereas RMF at 750 °C were higher. In particular, the cotton $T_{onset10\%}$, T_{max} and RMF in nitrogen (322 °C, 367 °C and 13%) passed to 278, 336 and 24% for COT/B-CYSS (add-on 12%), to 260, 312 and 20% for COT/BACYSS-GLY (add-on 18%) and to 272, 315 and 21% for COT/BACYSS-MP (add-on 18%) (Figure 6 and Table 3).

Table 3. Thermal data of SS-PAA-treated cotton fabrics from thermogravimetric analyses in nitrogen and air.

Sample	Add-on%	$T_{onset10\%}$ [°C]	T_{max1}[a] [°C]	T_{max2}[a] [°C]	RMF[d] at 750 °C [wt.-%]
Nitrogen					
COT	-	322	367	-	13.0
COT/B-CYSS	12	278	336	-	24.0
COT/BACYSS-GLY	18	260	312	-	20.0
COT/BACYSS-MP	18	272	315	-	21.0
Air					
COT	-	304	347[b]	480	-
COT/B-CYSS	12	274	324[b]/*414*[c]	453	4.0
COT/BACYSS-GLY	18	260	309[b]	499	5.0
COT/BACYSS-MP	18	264	306[b]	490	4.0

[a] From dTG curve; [b] main decomposition; [c] temperature at intermediate decomposition step (T_{int}) peculiar of COT/B-CYSS; [d] Residual Mass Fraction.
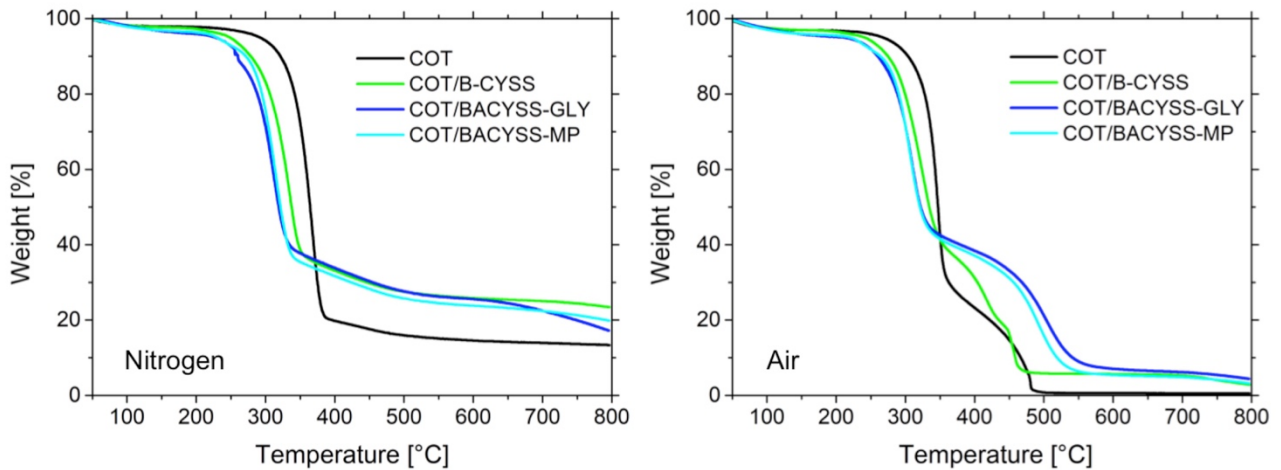

Figure 6. TG thermograms of SS-PAA treated cotton in nitrogen and air. Add-on values: COT/B-CYSS 12%, COT/BACYSS-GLY and COT/BACYSS-MP 18%.

In air, the TG thermograms of both untreated- and SS-PAA treated cotton were more complex than those in nitrogen, showing two (COT/BACYSS-GLY and COT/BACYSS-MP) or three (COT/B-CYSS) inflection points instead of a single inflection (Figure 6). It may be observed that the thermograms of both COT/BACYSS-GLY and COT/BACYSS-MP had lower $T_{onset10\%}$ and T_{max1}, but significantly higher T_{max2} than cotton. COT/B-CYSS stood apart. It had lower $T_{onset10\%}$, T_{max1} and

T_{max2} than cotton, nevertheless, as the other COT/SS-PAA-treated samples, left significant (4-5%) RMF at 750 °C. As for SS-PAAs, the TG traces in air of SS-PAA treated cotton showed a significantly lower mass loss between 350 and 450 °C than those in nitrogen.

3.6. Combustion tests

3.6.1. Horizontal flame spread tests

Horizontal flame spread tests were performed on 20 x 50 mm^2 strips of cotton fabrics treated with SS-PAAs at add-ons in the range 12-18%. The snapshots relative to SS-PAA treated cotton at different combustion steps are shown in Figure 7 and the combustion data reported in Table 4.

At 12% add-on COT/B-CYSS did not ignite but only afterglow was observed for ~ 40 s, leaving 96% residual mass fraction (RMF). At the same add-on, COT/BACYSS-GLY specimens ignited but self-extinguished in ~ 20 s, leaving ~ 81% RMF (Figure S1a in Supplementary material), whereas COT/BACYSS-MP ignited and almost completely burnt for ~ 60 s, leaving a thin residue (Figure S1b). At 18% add-on, neither COT/BACYSS-GLY nor COT/BACYSS-MP ignited, but underwent afterglow for 30 and 22 s, leaving 94 and 93% RMF, respectively. In all cases a very small specimen area burnt at a very low combustion rate. Comparing the FR performance of SS-PAAs, it may be observed that the disulfide group location plays a role. Indeed, the disulfide groups located in the amine-derived subunit (B-CYSS) did not ignite at add-on 12%, whereas disulfide groups in the bisacrylamide subunit turned out to be still effective, albeit to a minor extent. In fact, BACYSS-GLY did not ignite and BACYSS-MP ignited but after 1 s extinguished flame at 18% add-on.
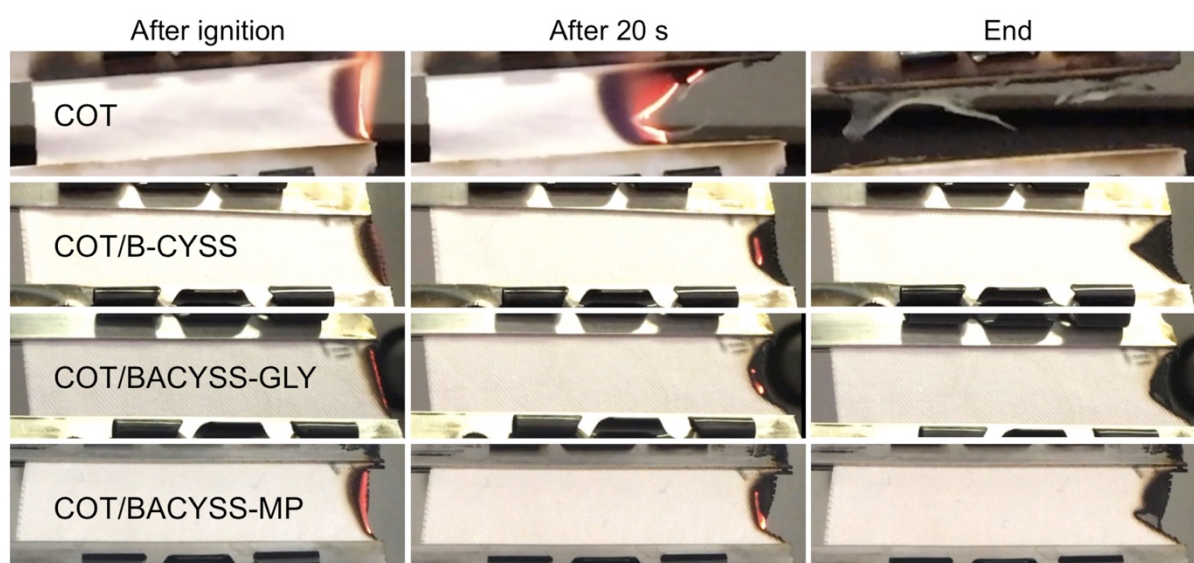

Figure 7. Snapshots of untreated and SS-PAA treated cotton in horizontal flame spread tests. Add-on values: COT/B-CYSS 12%; COT/BACYSS-GLY and COT/BACYSS-MP 18%.

Table 4. Combustion data of SS-PAA treated cotton from horizontal flame spread tests.

Sample	Add-on [wt.-%]	Note	Combustion		Char length[b] [mm]	Extinguishment [YES/NO]	RMF[c] [wt.-%]
			time[a] [s]	rate [mm s⁻¹]			
COT	-	-	52	1.0	-	NO	-
COT/B-CYSS	12	No flaming, only afterglow	40		7	YES	96
COT/BACYSS-GLY	12	10 s flaming followed by afterglow	36	0.2	6	YES	81
COT/BACYSS-GLY	18	No flaming, only afterglow	30		5	YES	94
COT/BACYSS-MP	12	Flaming	60	0.8	50	NO	36
COT/BACYSS-MP	18	1 s flaming followed by afterglow	22	0.2	4	YES	93

[a] ± 2 s; [b] ± 2 mm; [c] ± 1 wt.-%.

3.6.2. Vertical flame spread tests

Vertical flame spread tests were performed on strips of cotton fabrics treated with SS-PAAs at add-on values sufficient, case by case, to inhibit ignition (12% for B-CYSS and 18% for BACYSS-GLY) or extinguish flame (18% for BACYSS-MP) in horizontal configuration tests. The related snapshots at different combustion steps are reported in Figure 8, whereas the results are listed in Table 5.

COT/B-CYSS at 12% add-on did not ignite, but underwent a modest afterglow consuming a limited specimen area (Figure 8) and leaving 76% RMF (Table 5). COT/BACYSS-GLY and COT/BACYSS-MP at 18% add-on did not inhibit ignition, but in both cases the flame glided on a portion of the specimen surface and disappeared in about 18 s. Subsequently, the specimens were slowly consumed by afterglow leaving non-coherent, but considerable RMF values (20 and 39%, respectively). Untreated cotton burnt completely leaving negligible residue. The flaming combustion times of COT/BACYSS-GLY and COT/BACYSS-MP were similar to that of cotton. However, their total combustion times, given by the sum of the flaming combustion times and the afterglow times, were much higher due to the long duration of the latter.
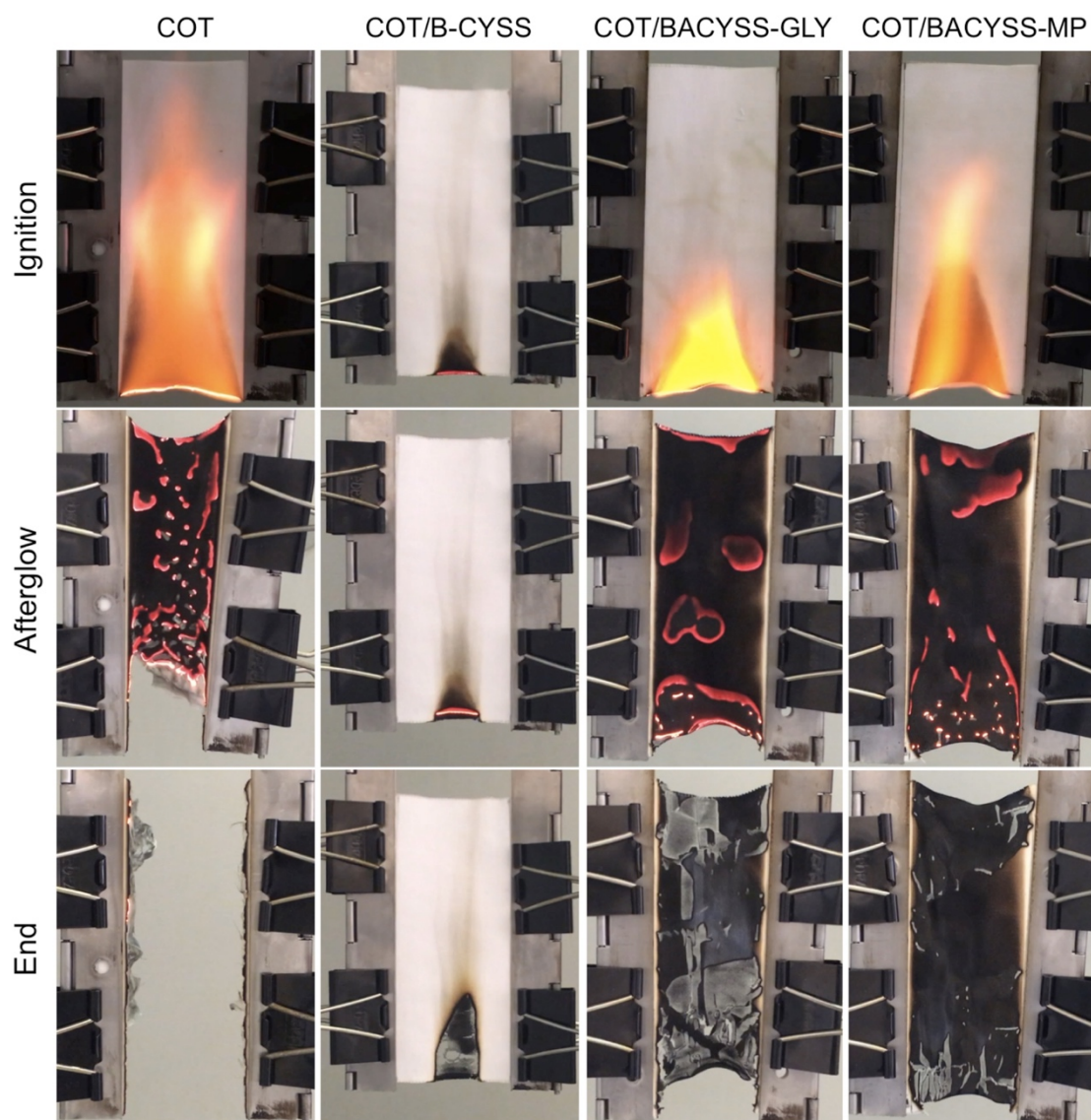
Figure 8. Snapshots of untreated and SS-PAA treated cotton in vertical flame spread tests. Add-on values: COT/B-CYSS 12%; COT/BACYSS-GLY 18%; COT/BACYSS-MP 18%.

Table 5. Combustion data of SS-PAA-treated cotton fabrics from vertical flame spread tests.

Sample	Add-on [%]	Flaming combustion		Afterglow combustion		Total combustion		Extinguishment [YES/NO]	RMF[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	NO	< 2
COT/B-CYSS	12	0	0	103	1.0	103	1.0	YES	76
COT/BACYSS-GLY	18	18	5.6	190	0.5	208	0.5	NO	20
COT/BACYSS-MP	18	17	6.1	79	1.4	96	1.0	NO	39

[a] ±1 s; [b] ±1 wt.-%.

SEM micrographs of the combustion residues of SS-PAA treated cotton fabrics (Figures 9 and 10) showed that in the case of samples subjected to a widespread afterglow (BACYSS-GLY and BACYSS-MP), the residue consisted of fibers partially consumed by flame exposure, but still oriented as in the original fabric (Figure 10). It may be observed that all fibers showed the presence of microbubbles testifying intumescence.
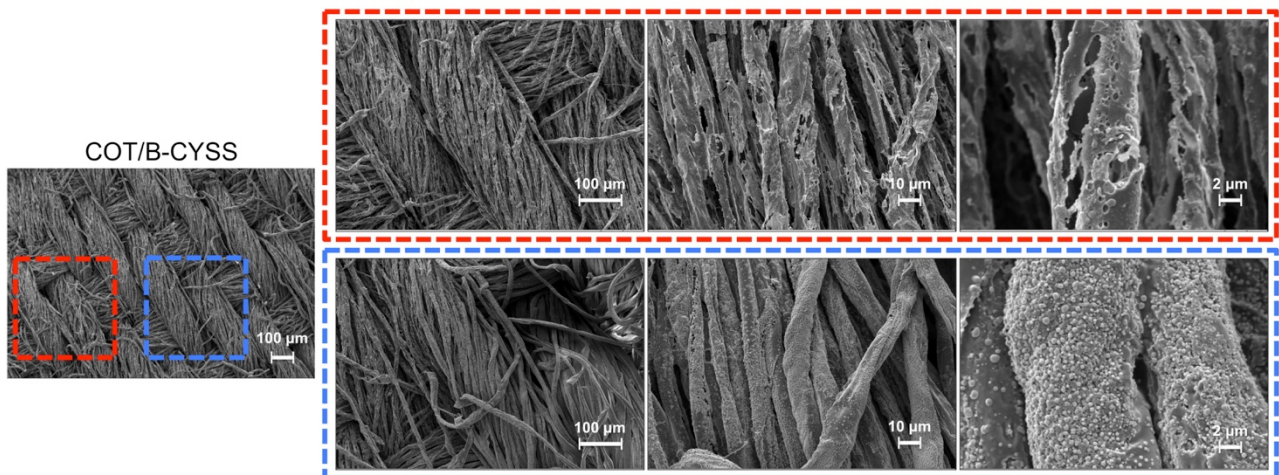

Figure 9. SEM magnification of COT/B-CYSS residue after vertical flame spread tests.
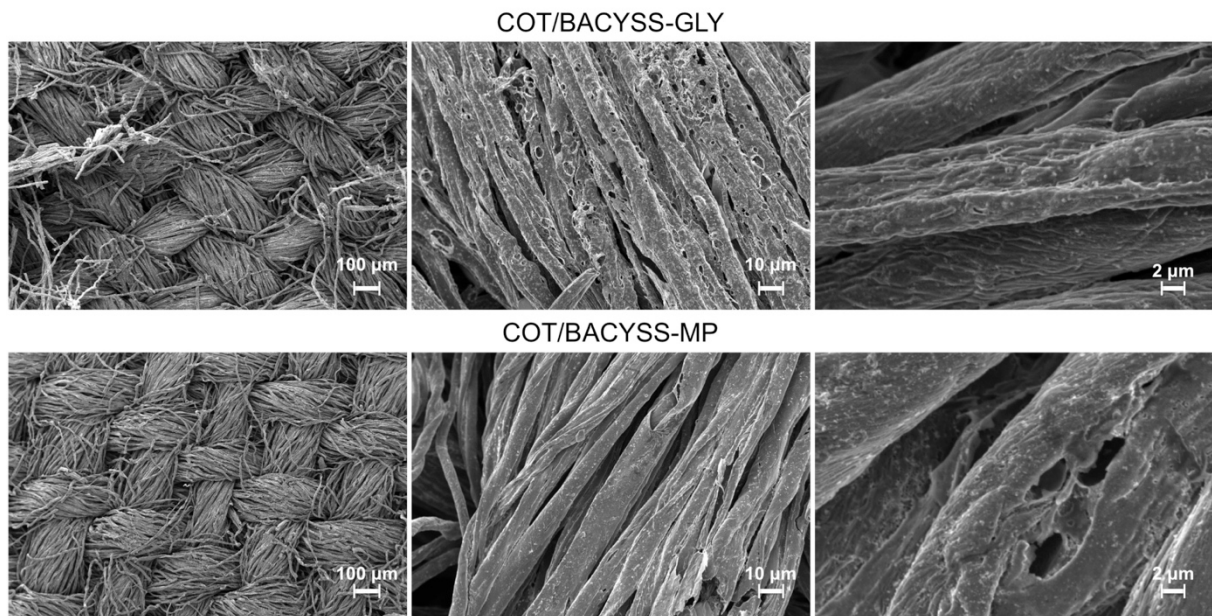

Figure 10. SEM magnification of COT/BACYSS-GLY and COT/BACYSS-MP residues after vertical flame spread tests.

The FT-IR/ATR spectra recorded on the combustion residues of vertical flame spread tests are reported in Figure 11. It may be observed that the broad band centered at 3360 cm^{-1} ascribable to residual cotton was not present in the spectrum of COT/B-CYSS. This was probably due to the fact that COT/B-CYSS did not ignite, and the spectrum was relative to the small amount of powder produced by the initial limited afterglow, whereas in the case of COT/BACYSS-GLY and COT/BACYSS-MP the analyzed products were the substantial residues of partial combustion (Figure 8). In the remaining part of the spectra, absorption bands were mostly attributable to aromatic thermal polycondensation products.
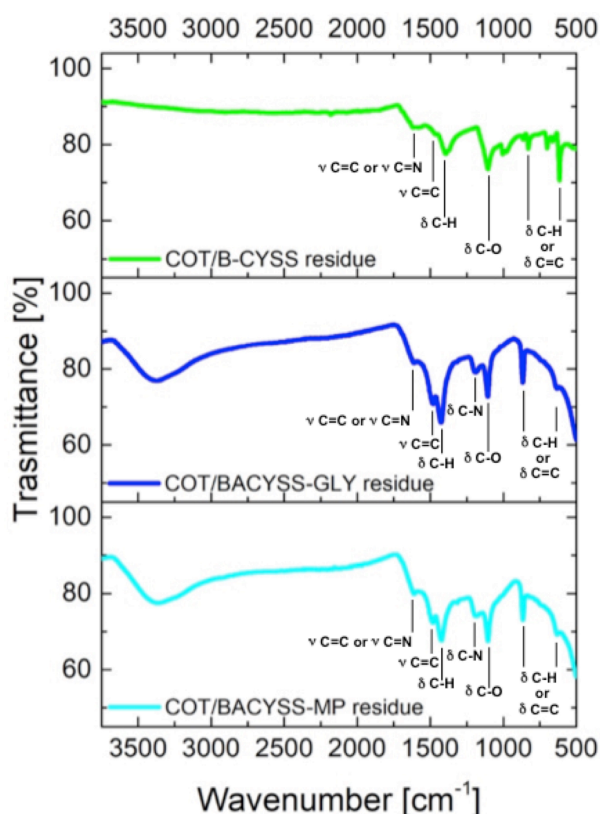

Figure 11. FT-IR/ATR spectra of SS-PAA treated cotton residues after vertical flame spread tests.

3.6.3. Cone calorimetry tests

Cone calorimetry tests were performed to simulate a realistic fire scenario.[19] In these tests, SS-PAA treated fabrics were exposed to a 35 kWm^{-2} heat flux, as usually found in developing fires, capable of bringing the sample surface to approximately 520 °C.[19] Samples underwent degradation and released combustible volatile gases, ultimately leading to ignition and subsequently flaming combustion. Combustion parameters such as time to ignition (TTI), peak of heat release rate (PHRR), effective heat of combustion of volatiles (EHC) and total heat release (THR) are reported

in Table 6. Figure 12 compiles the heat release rate (a), carbon monoxide (b) and dioxide curves (c) of untreated and SS-PAA treated cotton.

Table 6. Combustion data of SS-PAA treated cotton from cone calorimetry tests.[a]

Sample	Add-on [%]	TTI[a] [s]	PHRR[b] [kWm^{-2}]	ΔPHRR [%]	FPI[c] [sm^2 kW^{-1}]	EHC[d] [MJkg^{-1}]	ΔEHC [%]	THR[e] [MJm^{-2}]	RMF[f] [wt.-%]
COT	-	12±4	116±6	-	0.10±0.05	27.5±1.4	-	2.2±0.1	-
COT/B-CYSS	12	18±1	73±4	-37	0.25±0.05	14.2±0.7	-48	2.5±0.5	5.5±0.5
COT/BACYSS-GLY	18	22±1	51±2	-56	0.42±0.12	15.3±0.6	-44	2.0±0.1	8.0±0.5
COT/BACYSS-MP	18	23±1	57±3	-51	0.39±0.11	13.2±0.6	-52	2.0±0.1	8.5±0.5
COT/B-GLY	12	20±1	57±3	-51	0.36±0.12	13.1±0.6	-52	2.0±0.1	4.5±0.5
COT/B-MP[12]	18	22±4	82±4	-29	0.27±0.11	17.0±0.8	-38	2.7±0.1	2.0±0.5

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

All SS-PAAs increased cotton resistance to the employed heat flux, by significantly increasing TTI, decreasing EHC, and delaying and decreasing PHRR, while leaving significant RMF (Figure 13). No significant THR differences were found between untreated- and SS-PAA treated cotton. COT/B-CYSS showed the lowest TTI compared with the other SS-PAA treated cotton samples. EHC, representing the effective heat of combustion of volatiles per unit of mass loss,[19] were remarkably reduced following SS-PAA treatment (ΔEHC 44-52% with respect to cotton), with no significant difference among the members of the series. This showed that the amounts of combustible volatiles, hence the total fuel support of the flame was drastically reduced for SS-PAA treated cotton.

All SS-PAAs were equally effective in significantly delaying PHRR (Figure 12a). BACYSS-GLY and BACYSS-MP lead to higher ΔPHRR values than B-CYSS (-56 and -51% vs -37%), indicating that the disulfide groups present in the bisacrylamide subunits of SS-PAAs were, in this test, more effective than those in the amine subunits.

The fire performance index (FPI), defined as the TTI to PHRR ratio, was introduced as a parameter for assessing the FR efficacy.[18] According to the FPI data of Table 6, the efficacy as FR of SS-PAAs and their sulfur-deprived PAA analogues B-GLY and B-MP, prepared from 2,2-bis(acrylamido)acetic acid and, respectively, glycine and 2-methylpiperazine and previously studied

as FR,[12] should be ranked in the order: BACYSS-GLY>BACYSS-MP>B-GLY>B-MP>B-CYSS (0.42, 0.39, 0.36, 0.27 and 0.25, respectively). Paradoxically, this ranking almost totally disagreed with the actual fire retardant potency revealed by combustion tests, especially as regards the vertical ones. In fact, B-CYSS, capable to extinguish flame both in horizontal and vertical tests at 12% add-on, was ranked last, even after B-MP, unable to extinguish flame in both horizontal and vertical combustion tests at add-ons up to 30%.[12]

The FR activity of sulfur-deprived PAAs was mostly attributed to their intumescence on heating, producing a carbonaceous layer protecting the underneath cotton fibers.[12] Also SS-PAAs intumesced, but to a lesser extent, nevertheless in one case performed remarkably better in vertical combustion tests, inhibiting ignition and minimizing afterglow. By contrast, the best sulfur-deprived PAAs (B-GLY) performed somewhat better than B-CYSS in horizontal flame tests. This was probably due to the fact that SS-PAAs exerted a dual-mode FR action. From one side, they intumesced; from the other side, by analogy with keratin[1] and cystine,[20] they presumably gave off on heating hydrogen sulfide and sulfur radicals that quenched flame by interfering with radical oxidation processes occurring in the gas phase.[7] The latter mode of action explained their FR activity in vertical combustion tests, where the formed gaseous quenchers of radicals followed the flame along the tested specimen, but was scarcely evidenced in horizontal combustion tests, where the gaseous thermal decomposition products rose in air perpendicularly to the burning specimen, and could not be revealed in cone calorimetry tests, where the gaseous products were continuously sucked up and removed. The generally superior performance of B-CYSS in comparison with the other SS-PAAs might be due to easier H_2S release from disulfide groups located in the amine subunits (see also in Figure 6 the additional inflection point at 414 °C, T_{int}, peculiar of the TGA tracing of COT/B-CYSS). It may be noticed that the cystine moieties in B-CYSS preserved the amine character of cystine. Cystine may be released by thermally induced retro-Michael reaction, and is known to thermally decompose developing H_2S.[20]
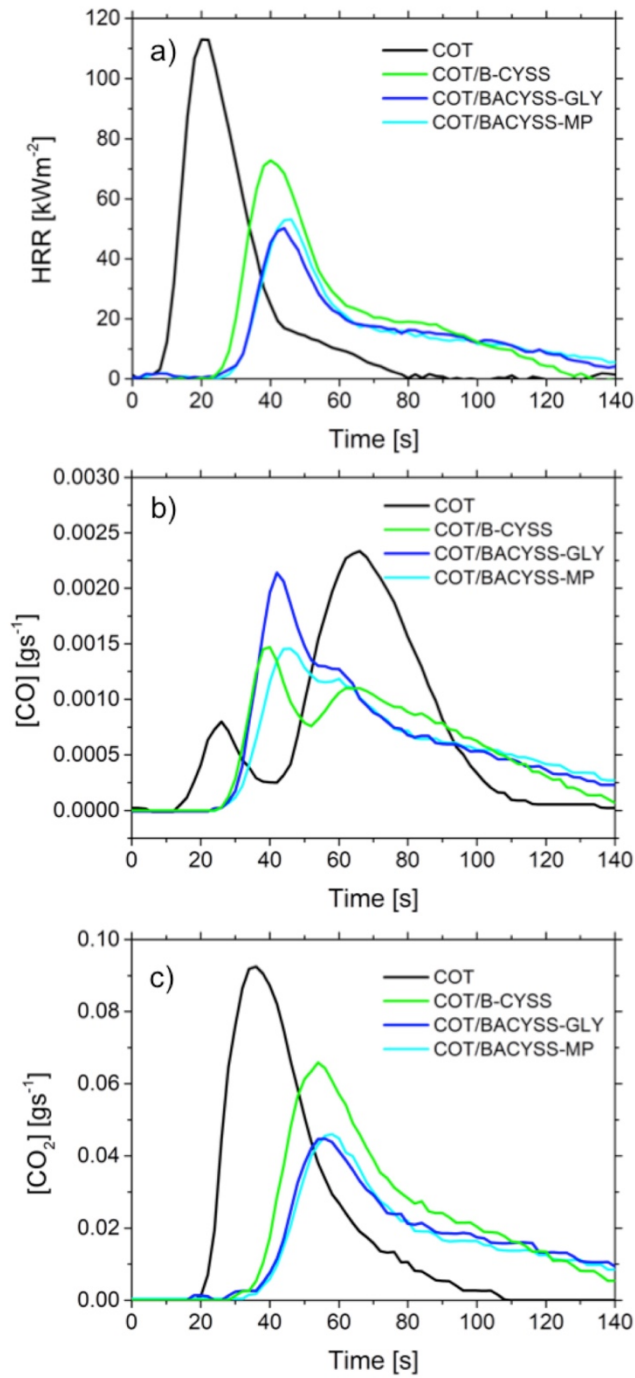
Figure 12. Results of cone calorimetry tests on SS-PAA-treated cotton fabrics: HRR time dependence (a); CO (b) and CO_2 (c) release curves.
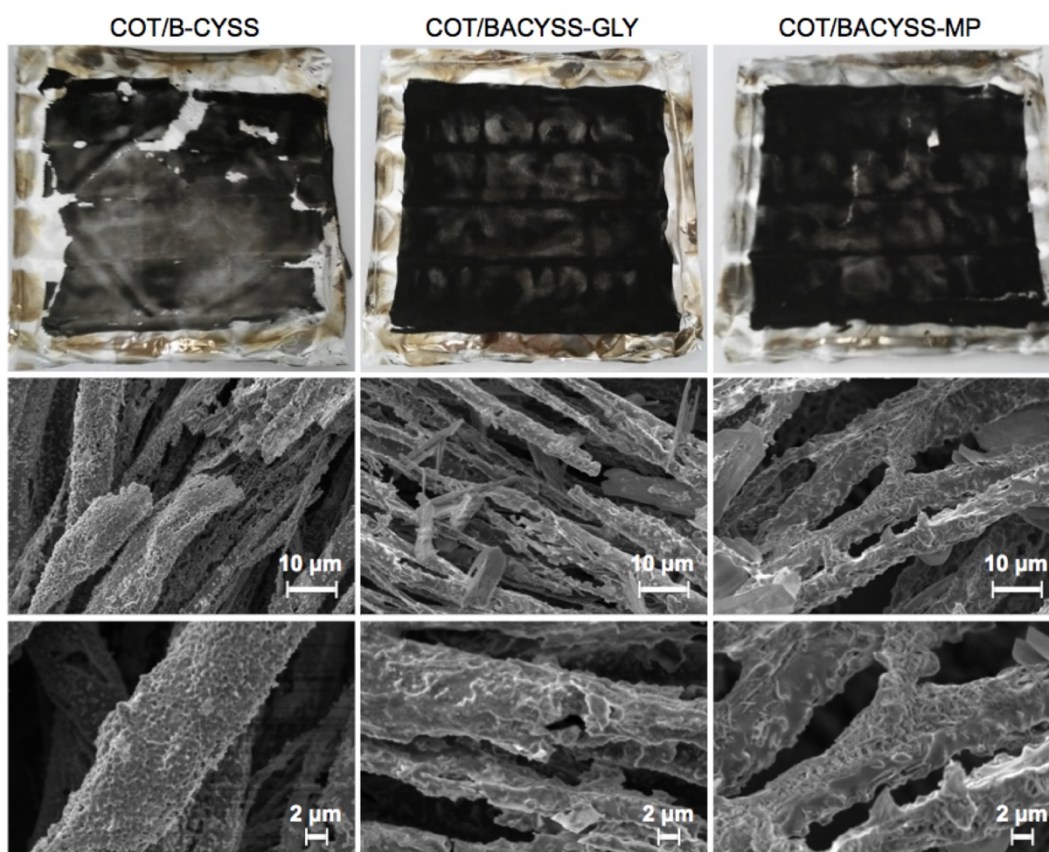
Figure 13. Morphology of SS-PAA treated cotton residues after cone calorimetry test: a) life size picture (1st row); b) SEM micrographs at different magnifications (2nd and 3rd rows).

The CO and CO_2 release curves of untreated and SS-PAA treated cotton are shown in Figures 12b and 12c, and the yields of both gases are listed in Table 7. Cotton CO release curve presented two peaks with maximum at 26 and 66 s, the highest peak occurring later, whereas CO_2 release curve showed an asymmetric single peak with maximum centered at 36 s. Overall, SS-PAA treatment caused significant reduction of both [CO] and [CO_2] yields, with Δ[CO] from 19 to 25% and Δ[CO_2] from 12 to 27% (Table 7) and changed the release patterns. In particular, the CO release curves (Figure 12b) showed two merging peaks, with maxima placed in between the time elapse of cotton maxima, that is, 40/64 s, 44/60 s and 46/60 s for COT/B-CYSS, COT/BACYSS-GLY, and COT/BACYSS-MP, respectively, vs 26/66 s for cotton. The first peak, placed the PHRR time (40, 44 and 46 s), was always more intense than the first peak of cotton curve. The second peak was much less pronounced than in cotton, becoming a shoulder of the first one in the case of BACYSS-GLY and BACYSS-MP, with a slow decrease of [CO] that never zeroed all throughout the experiment. As in the case of cotton, the CO_2 release curves of the SS-PAA treated cotton (Figure 12c) were characterized by a single peak with a significantly reduced area (12-27%, Table 7) with

respect to cotton, and a maximum value shifted from 36 s to 54-56 s. These maxima were placed at times very close to those of the second [CO] release peaks.

Table 7. [CO] and [CO_2] yields of SS-PAA-treated cotton fabrics from cone calorimetry.

Sample	Add-on [%]	[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-CYSS	12	0.0490±0.0024	-25	1.62±0.08	-14
COT/BACYSS-GLY	18	0.0513±0.0030	-22	1.68±0.08	-12
COT/BACYSS-MP	18	0.0526±0.0026	-19	1.38±0.07	-27

The SEM micrographs SS-PAA treated cotton residues after cone calorimetry test (Figure 13) revealed the presence of bubbles due to intumescence. Analogously to what observed in vertical flame spread tests, the residues of SS-PAA treated cotton samples after cone calorimetry tests consisted of fibers partially consumed by combustion due to the exposure to 35 kWm^{-2} heat flux, but still oriented following the original texture of cotton fabric. In the same test, plain cotton did not leave a significant residue.

The FT-IR/ATR spectra recorded on combustion residues after cone calorimetry tests are reported in Figure 14. These spectra showed nearly identical absorption bands as those of the combustion residues of vertical flame spread tests.
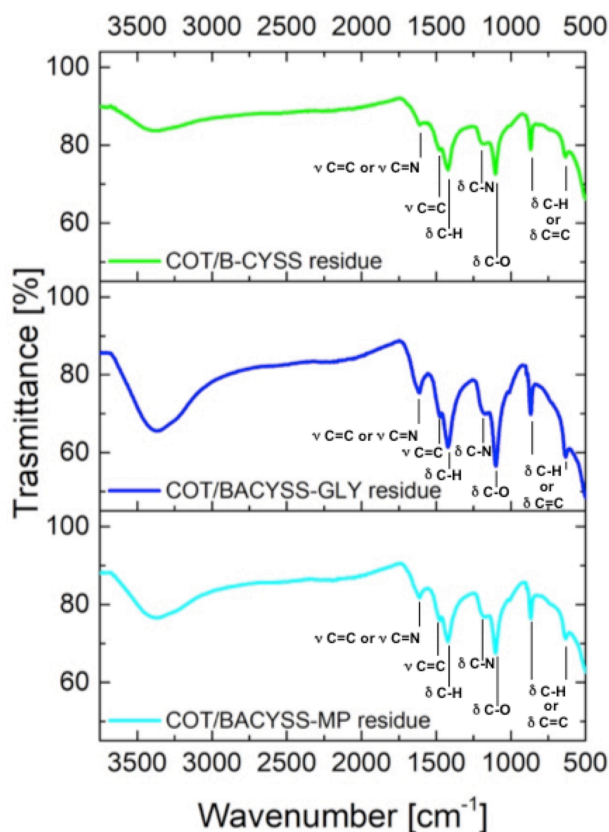
Figure 14. FT-IR/ATR of SS-PAA treated fabric residues after cone calorimetry tests.

4. Conclusions

On the whole, the introduction of disulfide groups in PAAs improved their flame retardant properties, specifically in vertical flame spread test, where B-CYSS inhibited ignition at 12% add-on. BACYSS-GLY and BACYSS-MP, even if did not extinguish flame at add-on values up to 18%, left in all cases heavy carbonaceous residues. No sulfur-deprived PAA showed a similar performance. In horizontal flame spread tests, B-CYSS inhibited ignition at 12% add-on, whereas BACYSS-GLY did not ignite and BACYSS-MP ignited but after 1 s extinguished flame at 18% add-on. In the same test, sulfur-deprived PAAs deriving from 2-methylpiperazine never extinguished flame up to at least 30% add-on.[12] By contrast, the 2-methylpiperazine deriving BACYSS-MP extinguished flame, albeit at a higher add-on (18%) than BACYSS-GLY. All results allowed concluding that the disulfide group was more effective if located in the amine subunit but still effective, even if to a minor extent, if located in the amide subunit. This was tentatively attributed to the easier release of H_2S in the former case where the cystine moieties were amenable to retro-Michael elimination reaction, since their amine character was maintained in the polymer chain.

Appendix A. Supplementary material

References

1. G. Sanchez-Olivares, A. Sanchez-Solis, F. Calderas, J. Alongi, Keratin fibres derived from tannery industry wastes for flame retarded PLA composites, Polym. Degrad. Stab. 140 (2017) 42-54.

2. G. Janowska, A. Kucharska-Jastrzabek, M. Prochon, A. Przepiorkowska, Thermal properties and combustibility of elastomer-protein composites, J. Therm. Anal. Calorim. 113 (2013) 933-938.

3. K. Wrześniewska-Tosik, S. Zajchowski, A. Bryśkiewicz, J. Ryszkowska, Feathers as a flame-retardant in elastic polyurethane foam, Fibres & Textiles in Eastern Europe 22 (2014) 119-128.

4. X.Y. Wang, C.Q. Lu, C.X. Chen, Effect of chicken-feather protein-based flame retardant on flame retarding performance of cotton fabric, J. Appl. Polym. Sci. 131 (2014) 40584.

5. J.R. Barone, W.F. Schmidt, C.F.E. Liebner, Compounding and molding of polyethylene composites reinforced with keratin feather fiber, Compos Sci. Technol. 65 (2005) 683-692.

6. M. Zhan, R.P. Wool, Mechanical properties of chicken feather fibers, Polym. Compos. 32 (2011) 937-944.

7. V. P. M., M. Poletto, Polypropylene-based biocomposites and bionanocomposites, John Wiley & Sons, 2017, pag. 162.

8. W. Pawelec, A. Holappa, T. Tirri, M. Aubert, H. Hoppe, R. Pfaendner, C.-E. Wilén, Disulfides Effective radical generators for flame retardancy of polypropylene. Polym. Degrad. Stab. 110 (2014) 447-456.

9. P. Ferruti, Polyamidoamines: past, present and perspectives, J. Polym. Sci.: Part A: Pol. Chem. 51 (2013) 2319-2353.

10. E. Jacchetti, E. Emilitri, S. Rodighiero, M. Indrieri, A. Gianfelice, C. Lenardi, A. Podestà, E. Ranucci, P. Ferruti, P. Milani, Biomimetic poly(amidoamine) hydrogels as synthetic materials for cell culture. J. Nanobiotechnology 6 (2008) 14.

11. N. Mauro, A. Manfredi, E. Ranucci, P. Procacci, M. Laus, D. Antonioli, C. Mantovani, V. Magnaghi, P. Ferruti, Degradable poly(amidoamine) hydrogels as scaffolds for in vitro culturing of peripheral nervous system cells, Macromol. Biosci. 13 (2013) 332-347.

12. A. Manfredi, F. Carosio, P. Ferruti, E. Ranucci, J. Alongi, Linear polyamidoamines as novel biocompatible phosphorus-free surface confined intumescent flame retardants for cotton fabrics, Polym. Degrad. Stab. 151 (2018) 52-64.

13. E. Emilitri, E. Ranucci, P. Ferruti, New poly(amidoamine)s containing disulfide linkages in their main chain, J. Polym. Sci. Pol. Chem. 43 (2005) 1404-1416.

14. E. Emilitri, P. Ferruti, R. Annunziata, E. Ranucci, M. Rossi, L. Falciola, P. Mussini, F. Chiellini, C. Bartoli, Novel amphoteric cystine-based poly(amidoamine)s responsive to redox stimuli, Macromolecules 40 (2007) 4785-4793.

15. P. Ferruti, E. Ranucci, F. Trotta, E. Gianasi, E.G. Evagorou, M. Wasil, G. Wilson, R. Duncan, Synthesis, characterisation and antitumour activity of platinum (II) complexes of novel functionalised poly(amido amine)s, Macromol. Chem. Phys. 200 (1999) 1644-1654.

16. J. Tata, J. Alongi, F. Carosio, A. Frache, Optimization of the procedure to burn textile fabrics by cone calorimeter: part I. Combustion behavior of polyester, Fire Mater. 35 (2011) 397-409.

17. ISO 5660, Fire Test, Reaction to Fire, Rate of Heat Release (Cone Calorimeter Method), International Organization for Standardization, Geneva, 2002.

18. B. Schartel, M. Bartholomai, U. Knoll, Some comments on the main fire retardancy mechanisms in polymer nanocomposites, Polym. Adv. Technol. 17 (2006) 772-777.

19. B. Schartel, R. Hull, Development of fire-retardant materials-interpretation of cone calorimeter data, Fire Mater. 31 (2007) 327-354.

20. Y. Mori, F. Akagi, A. Yajima, T. Kitagawa, Thermal decomposition of solid amino acids in relation to their hydrogen bonds. I. Kinetic studies on the thermal decomposition of solid cystine, Chem. Pharm. Bull. 33 (1985) 916-926.

TABLE OF CONTENT