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Layer by Layer ammonium polyphosphate-based coatings for flame retardancy of polyester–cotton blends

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ABSTRACT

Ammonium polyphosphate (APP)-based coatings have been prepared through Layer by Layer deposition, in order to enhance the thermal stability in air and the flame retardancy properties of polyester–cotton blends. To this aim, two different counterparts, i.e. chitosan molecules and silica nanoparticles, have been coupled with APP. These species have been selected in order to prepare two novel flame retardant systems based on a different action mechanism. Indeed, the chitosan–APP pair represents an intumescent-like system, in which chitosan can act as both carbon source and foaming agent, whereas APP produces in situ phosphoric acid at high temperatures, favouring the char formation. On the other hand, the silica–APP pair exploits the joint effect between the phosphoric acid generated by APP that induces the carbonization of the polymer, and the thermal insulator behaviour of a ceramer such as silica. The two systems under study turned out to be responsible of an overall enhancement of the flame retardancy. Indeed, both the coatings were able to suppress the afterglow phenomenon and to leave a remarkable residue after the flammability test. In the case of chitosan-based assemblies, the residue appeared more coherent than that left by silica. Furthermore, silica/APP system showed a significant increase of the time to ignition and a strong decrease of the total heat release during cone calorimeter tests.

1. Introduction

Nowadays, fabric flammability still represents a severe threat for the safety of people and buildings. For this reason, since 1950, scientists have been continuously developing flame retardant treatments able to enhance the fabric resistance to flame; meanwhile, governments started worrying about the possible environmental and health risks related to the use of certain types of flame retardants. As a result, in the last 30 years, most of the high-performing flame retardants developed in the early 1950–1980 have been banned from commercial use or limited as far as their application field is concerned (Horrocks, 2011). In this context, different problems arise from the use of natural and synthetic fibres: the former can catch fire very easily and burn with vigorous flame, whereas the latter can melt during combustion, leading to the formation of incandescent drops that are able to spread the fire to other ignitable materials. As a consequence, the industrial and academic research activities are currently being exploited for developing efficient flame retardant systems for blends of natural and synthetic fibres, since this issue is also of very considerable economic importance.

Despite of the great efforts, no practical solution has been found yet. Lewin has thoroughly reviewed the main combustion features related to cotton and polyester blended in a single substrate (Lewin, 2005). Indeed, during its thermal decomposition, cotton carbonization results in char formation at low temperatures; at the same time, polyester melts (at 260 °C) and drips remaining dispersed between the charred cotton fibres. In details, cotton represents the initial source of fuel, since it decomposes earlier than polyester. This latter provides additional fuel to the gaseous phase at the high temperatures produced by the combustion of cotton. Lewin has also proposed the melt blending of different flame retardant species during the production of polyester fibres. Furthermore, the use of two different additives for protecting each fibre has been proposed, as well (Lewin, 1984). Alternatively, an intumescent system made of an acrylic binder resin and ammonium polyphosphate has been applied to polyester–cotton blends via back coating (Drevelle et al., 2005).

This difficult scenario opened the way for novel and non-conventional procedures such as surface modifications achieved by means of nanotechnology-inspired methods.

The present paper describes a different strategy focused on self-assembled surface adsorption in order to build simple architectures able to enhance the flame retardancy of polyester–cotton blends. This novel approach, as applied to textile substrates, consists in a multi-step adsorption process known as Layer by Layer (LbL) assembly; such a process has already been exploited by our group

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aiming to build complex hybrid organic–inorganic or completely inorganic nanoarchitectures on polyester fabrics (Carosio, Alongi, & Malucelli, 2011; Carosio, Laufer, Alongi, Camino, & Grunlan, 2011). The LbL technique, in its simpler application, consists in an alternate immersion of the substrate in oppositely charged polyelectrolyte solutions or suspensions; this process leads to the formation of positively and negatively charged layers (bilayers) piled up on the substrate surface and bonded by electrostatic attraction at the nanometric level (Decher & Hong, 1991). Recently, this approach turned out to be extremely advantageous when applied to cotton: Grunlan and coworkers have demonstrated that this technique can enhance the flame retardancy of cotton, using a branched polyethylenimine coupled to sodium cloisite (Li et al., 2010), silica nanoparticles (Laufer, Carosio, Martinez, Camino, & Grunlan, 2011) or polyhedral oligomeric silsesquioxanes (Li, Mannen, Schulz, & Grunlan, 2011). The results by flame vertical tests (according to ASTM D6413) and microcone calorimetry seem to be encouraging and promising.

In the present work, ammonium polyphosphate (APP)-based assemblies have been prepared through LbL deposition aiming to enhance the thermal stability in air and the flame retardancy properties of polyester–cotton blends (assessed by thermogravimetric analyses, combustion and flammability tests, respectively). To this aim, two different positively charged counterparts, i.e. chitosan molecules and silica nanoparticles, have been coupled with negatively charged APP.

More specifically, the chitosan–APP pair represents an intumescent-like system, in which chitosan can act as both carbon source and foaming agent, whereas APP is able to generate directly in situ phosphoric acid at high temperatures. As a consequence, chitosan dehydrates in the presence of this acid source, generating water vapour, favouring the char formation and thus significantly enhancing the polymer resistance towards combustion. On the other hand, the silica–APP pair exploits the joint effect between phosphoric acid (generated by APP) and the silica nanoparticles. The former can induce the carbonization of the polymer and the latter can act as physical surface barrier (i.e. *thermal insulator*) able to limit the heat, fuel and oxygen transfer between the flame and the polymer(s).

Finally, a correlation between the structure/morphology of the LbL assemblies (carried out by scanning electron microscopy and attenuated total reflectance spectroscopy) and the final properties of the polyester–cotton blend has been thoroughly discussed.

2. Experimental

2.1. Materials

Polyester–cotton fabrics (28 and 72%, PET-CO) with a density of 340 g/m^2 were kindly supplied by Antecuir SA (Alicante, Spain).

Ammonium polyphosphate (APP), chitosan (Chi, low molecular weight, presumable <20,000 Da) and water suspensions (30 wt.%) of positive alumina-coated silica nanoparticles were purchased from Sigma–Aldrich (Milwaukee, WI). All the products were used for preparing 0.2 wt.% solutions (APP or Chi) and suspensions (silica) for LbL assembly, using 14.6 μS deionized water supplied by a Q20 Millipore system (Milano, Italy). The pH of the Chi solution was adjusted to 3.5 using acetic acid (Sigma–Aldrich).

2.2. Layer by Layer deposition

PET-CO substrates were alternately immersed into negatively (APP) and positively (Chi or Silica) charged baths. After each immersion step, the substrate was washed with deionized water to remove the excess of ionic species. The immersion period for the first couple of layers was set at 10 min, in order to promote and achieve a uniform deposition; the subsequent layers were obtained after 5 min dipping. The process was repeated until 5, 10 and 20 bilayers (BL) were built for each system.

2.3. Characterization techniques

The growing of the architectures deposited through LbL was evaluated by attenuated total reflectance (ATR) spectroscopy. ATR spectra were recorded at room temperature in the range 4000–600 cm^{-1} (16 scans and 4 cm^{-1} resolution), using a Frontier FT-IR/FIR spectrophotometer, equipped with a Ge crystal.

The surface morphology of the treated samples was studied using a LEO-1450VP Scanning Electron Microscope (beam voltage: 20 kV); a X-ray probe (INCA Energy Oxford, Cu-K$_\alpha$ X-ray source, k = 1.540562 Å) was used to perform elemental analysis. Fabric pieces (5 mm × 5 mm) were cut and fixed to conductive adhesive tapes and gold-metallized.

The thermal and thermo-oxidative stability of the fabrics was evaluated by thermogravimetric (TG) analyses in nitrogen and in air, respectively, from 50 to 800 °C with a heating rate of 10 °C/min. A TAQ500 analyser was used, placing the samples in open alumina pans (ca. 10 mg), in inert or oxidative atmosphere (gas flow: 60 ml/min).

In order to describe a realistic fire scenario, it is important to test both the ignitability of a sample in the presence of a flame spread (flammability) and the combustion behaviour of the same sample under the irradiative heat flow developed as a consequence to the flame exposure. Therefore, the flame retardancy properties of the prepared samples were measured according to two different tests. The flammability test in vertical configuration was carried out by applying a propane flame for 5 s at the bottom of a fabric specimen (50 mm × 100 mm). The test was repeated 3 times for each formulation in order to get reproducible data, measuring burning time, afterglow time and the final residue. Furthermore, cone calorimetry (Fire Testing Technology, FTT) was employed to investigate the combustion behaviour of square samples (100 mm × 100 mm × 0.5 mm) under an irradiative heat flow of 35 kW/m^2 in horizontal configuration, following the procedure described elsewhere (Tata, Carosio, Alongi, & Frache, 2010). The fabrics were placed in a sample holder and maintained in the correct configuration by a metallic grid. Time to ignition (TTI, s), total heat release (THR, kW/m^2), heat release rate and corresponding peak (pkHRR, kW/m^2) were measured. Total smoke release (TSR, m^2/m^2), smoke production rate (SPR, m^2/s), peak of CO and CO$_2$ release (ppm and %, respectively) were evaluated, as well. For each sample, the experiments were repeated four times in order to ensure reproducible and significant data. The experimental error was evaluated as standard deviation (σ).

3. Results and discussion

3.1. Attenuated total reflectance

The formation of LbL assemblies has been qualitatively assessed by ATR spectroscopy.

Fig. 1 plots the ATR spectra of the pure APP and Chi (Fig. 1a), pure PET-CO blend and fabrics treated with Chi/APP (Fig. 1b) and silica/APP (Fig. 1c). Chi spectrum shows the presence of signals attributable to OH groups (3450 cm^{-1}), NH vibrations (stretching and bending at 3360 and 1590 cm^{-1}), CH$_2$ groups (symmetric or asymmetric stretching vibrations of the pyranose ring at 2920, 2876, 1419, 1319 cm^{-1}) and —C—O—C— in glycosidic linkage (1074 and 1030 cm^{-1}) (Pawlak & Mucha, 2003).

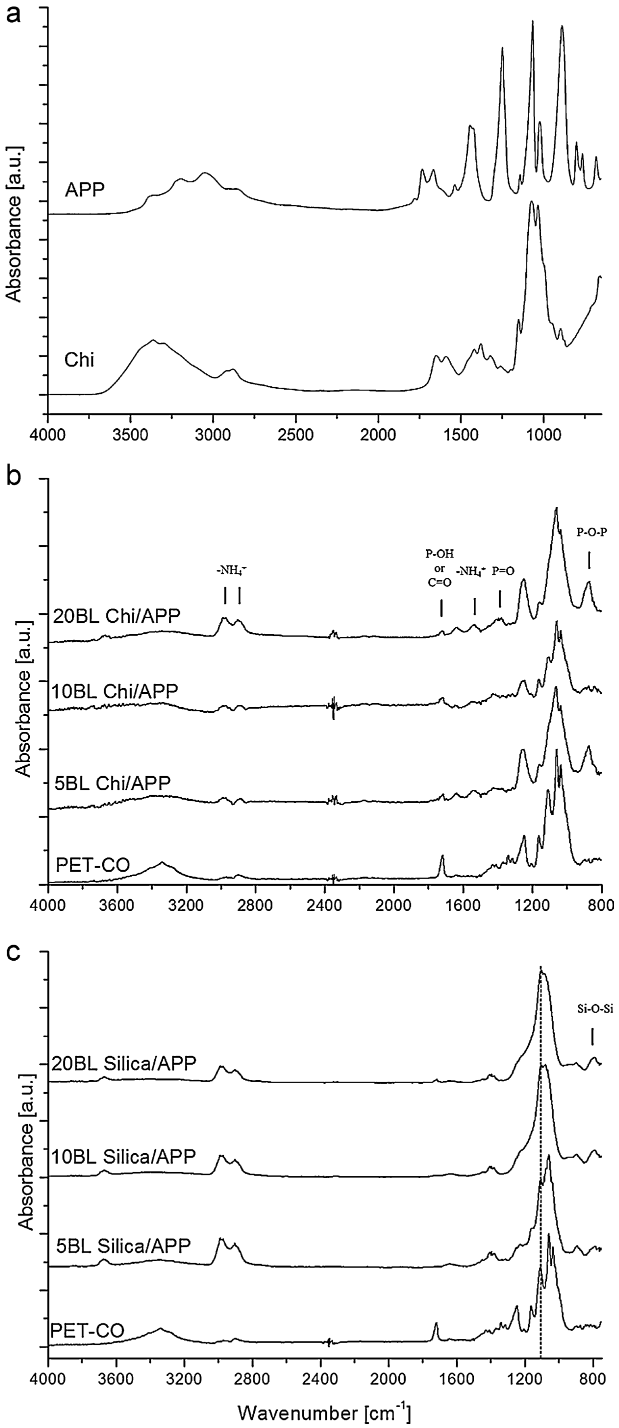

Fig. 1. ATR spectra of pure chitosan and APP (a), polyester–cotton blend and chitosan/APP- (b) and silica/APP-treated fabrics (c).

APP evidences the typical signals of ammonium group stretching and bending at 3100, 3050 and 1400 cm^{-1}, P—OH, P=O and P—O—P vibrational modes (at 1700, 1250 and 870 cm^{-1}, respectively) (Drevelle et al., 2005).

PET-CO spectrum shows a broad absorption band over 3600–3000 cm^{-1} (hydrogen bonded OH stretching) and a peak at around 2900 cm^{-1} (C—H stretching of alkyl chains), both attributable to infrared absorption frequencies of untreated cotton (Rosace & Massafra, 2008). In addition, the carbonyl group of polyester is evident at ca. 1720 cm^{-1}.

The spectra of the samples treated with Chi/APP (Fig. 1b) show a weak signal of the OH groups, indicating the presence of the deposited assembly on the surface of the blend.

Because of their saccharide nature, the signals of chitosan are not distinguishable from those of cotton; nevertheless, some typical signals of APP can be observed. Indeed, a weak signal is still visible at 1700 cm^{-1} in the treated fabrics that could be attributable to the P—OH group, as well as to the carbonyl group of polyester, the intensity of which decreases by increasing the number of bilayers. In the 1500–1000 cm^{-1} region many overlapped signals are present: however, the two signals at ca. 1250 and 870 cm^{-1} referring to P=O and P—O—P vibrational modes of APP are present, together with the typical peaks of ammonium group stretching and bending. These signals slightly shift to lower wavenumbers probably because the APP is confined within the architecture deposited on the fabrics.

As far as silica/APP assemblies are concerned (Fig. 1c), it is possible to observe the same peaks already discussed, which refer to APP. In addition, a peak at ca. 800 cm^{-1}, related to Si—O bending, points out the presence of the silica on the fabric surface. Finally, it is noteworthy the change of the shape of the signals in between 1400 and 800 cm^{-1}: indeed, by increasing the number of BL, the peaks overlap in a single signal.

3.2. Morphology

In order to assess the morphology of the fibres after the LbL treatment, SEM observations have been carried out. Fig. 2a and b shows the typical morphology of the untreated PET-CO blend at two different magnifications: the surface appears smooth and clean. When 5 (Fig. 2c and d), 10 (Fig. 2e and f) and 20 (Fig. 2g and h) Chi/APP bilayers are deposited on the blend, the fibre surface becomes rough since the fibres result completely and homogeneously covered by the assembly. No cracks are present in such systems because of the flexible feature of chitosan. From an overall morphological observation, it is not possible to distinguish remarkable differences among the three deposited architectures; nevertheless, the 20BL assembly shows the formation of some islands of Chi/APP grown on the surface.

As far as silica/APP systems are considered, the morphology of the fibres appears completely different. Indeed, even though the replacing of chitosan with silica (Fig. 3) favours the complete covering of the fibres, the resulting assembly appears to be thicker and more rigid with respect to that observed in the Chi/APP system. In particular, at 5BL (Fig. 3a and b) the coating appears continuous and homogenous, while at 10 (Fig. 3c and d) and 20 (Fig. 3e and f) bilayers several cracks appear due to the ceramic character of silica. This morphology strongly affects the thermal stability in air and the flame retardancy properties of the blend, as it will be discussed in the following paragraphs.

3.3. Thermal stability

The thermal and thermo-oxidative stability of the systems under study have been investigated by thermogravimetric analyses in nitrogen and air, respectively. The collected data are summarized in Tables 1 and 2.

Fig. 4a shows the weight loss and the corresponding rate of the pure blend and of the fabrics treated with Chi/APP in nitrogen (both TG and dTG curves). The pure blend degrades similarly to a typical polymer blend: indeed, its thermal degradation consists of two independent steps. The former refers to cotton (354 °C) and the latter to polyester (410 °C). When the fabric is treated with Chi/APP, it is possible to observe a strong anticipation of the decomposition process, as pointed out by the $T_{\mathrm{onset}5\%}$ values (Table 1). This anticipation can be likely ascribed to the presence of hydroxyl groups in the chitosan molecules that are able to catalyse the thermal

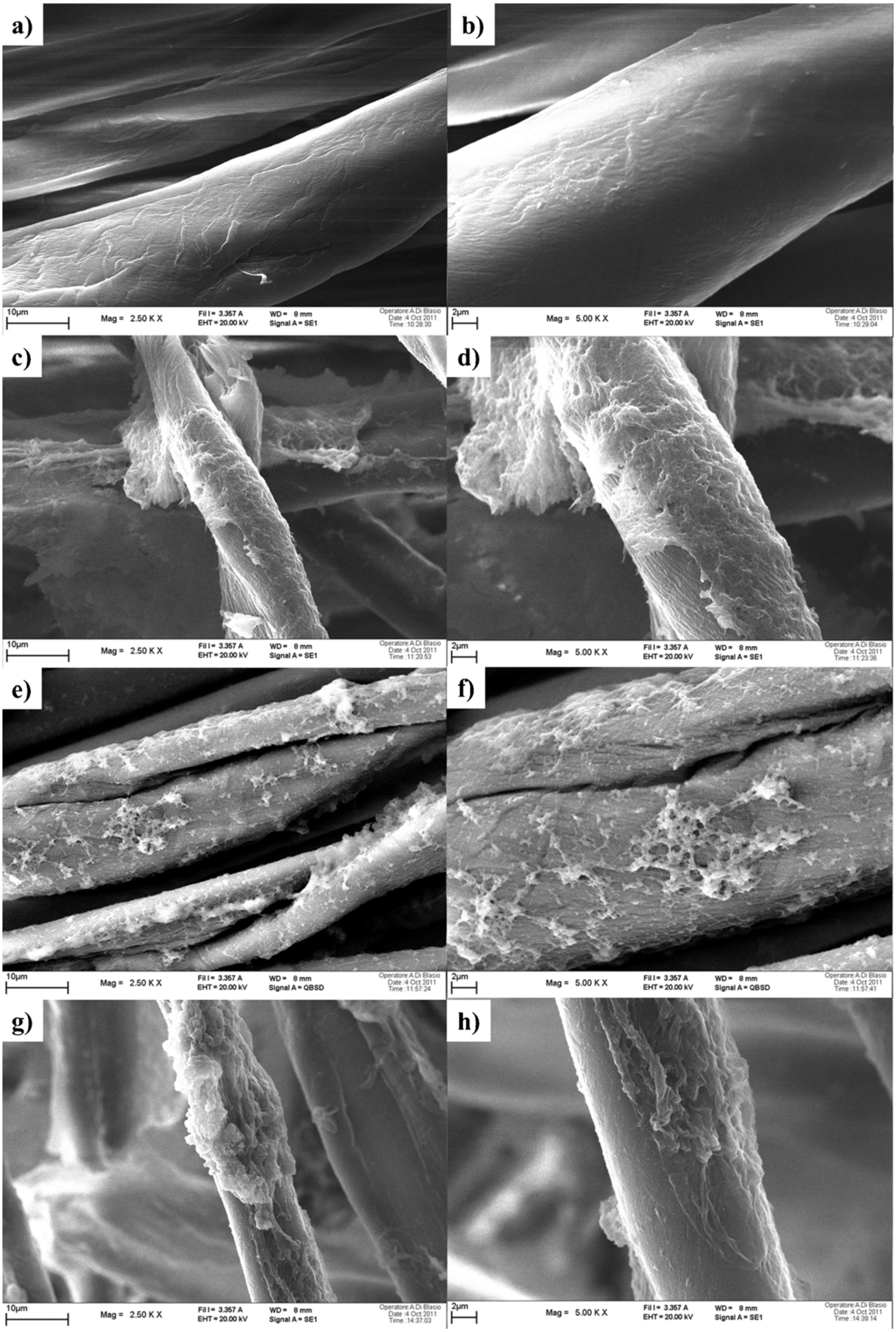

Fig. 2. SEM magnifications of pure polyester–cotton blend and chitosan/APP-treated fabrics.

decomposition of cotton, as already described in the literature (Xie et al., 2001). Furthermore, the effect of the water absorbed by Chi macromolecules or entrapped within the assemblies that could promote the hydrolytic degradation of polyester should be also taken into account. Indeed, by increasing the BL number, the chitosan content increases and consequently the $T_{\mathrm{onset}5\%}$ decreases. In addition, it is well documented in the literature the same effect induced by the presence of APP (Horrocks, 2011). Although this

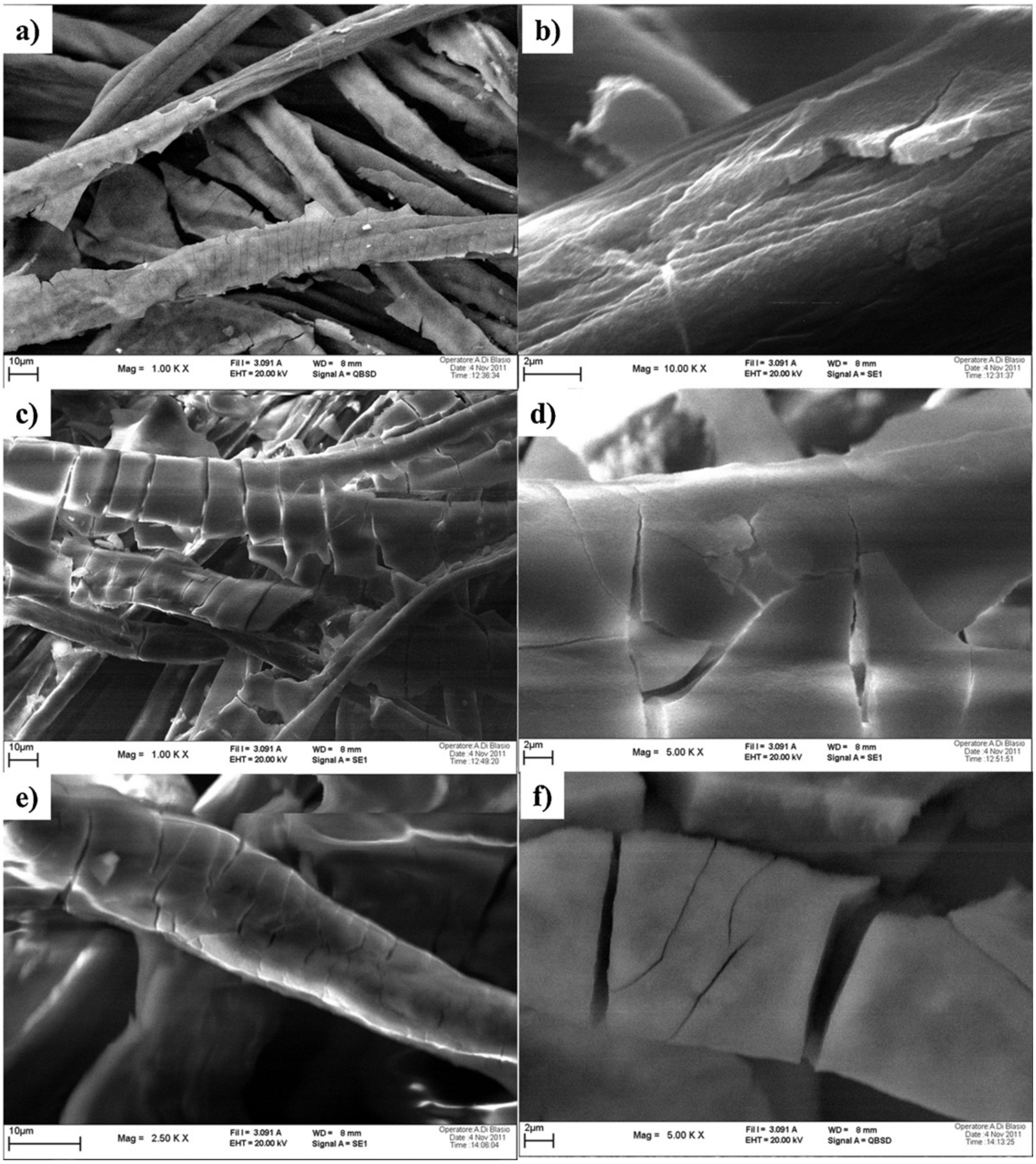

Fig. 3. SEM magnifications of silica/APP-treated fabrics.

could be a detrimental effect, an anticipation induced by APP could be extremely advantageous since it promotes the formation of a thermally stable carbonaceous structure (char) at lower temperatures (instead of the formation of volatile species), limiting the further degradation and/or combustion of the polymer blend (Horrocks, 2011). As a consequence, the first degradation step (which refers to cotton) is always anticipated for the treated fabrics (318, 312 and 310 °C for 5, 10 and 20BL vs. 354 °C—pure blend) and the residue registered at $T_{\max1}$ is lower than that of the pure blend (Table 1). On the contrary, the second step is postponed for the

Table 1
TGA data of pure and LbL treated fabrics in nitrogen.

Sample	$T_{\text{onset5\%}}$ (°C)	$T_{\max1}$[a] (°C)	$T_{\max2}$[a] (°C)	Residue at $T_{\max1}$ (%)	Residue at $T_{\max2}$ (%)	Residue at 700 °C (%)
PET-CO	274	354	410	56.2	29.7	14.7
5BL Chi/APP	275	318	430	45.4	36.3	16.0
10BL Chi/APP	260	312	431	49.3	40.0	19.7
20BL Chi/APP	258	310	429	50.4	41.0	20.9
5BL silica/APP	312	358	423	66.7	23.6	11.3
10BL silica/APP	312	356	421	63.5	23.7	11.8
20BL silica/APP	300	336	411	37.9	24.1	3.7

[a] From derivative curves.

Table 2
TGA data of pure and LbL treated fabrics in air.

Sample	$T_{onset5\%}$ (°C)	T_{max1}[a] (°C)	T_{max2}[a] (°C)	T_{max3}[a] (°C)	Residue at T_{max1} (%)	Residue at T_{max2} (%)	Residue at T_{max3} (%)	Residue at 700 °C (%)
PET-CO	292	343	411	499	61.3	25.4	5.9	2.0
5BL Chi/APP	268	311	419	515	48.5	33.6	14.0	4.1
10BL Chi/APP	260	306	421	520	51.3	37.0	15.8	4.1
20BL Chi/APP	253	303	422	523	53.0	38.5	16.1	3.3
5BL silica/APP	295	338	407	501	42.4	19.8	4.8	2.5
10BL silica/APP	301	338	411	507	48.2	22.9	6.9	3.4
20BL silica/APP	299	336	411	507	44.4	23.4	8.1	4.6

[a] From derivative curves.

treated fabrics: indeed, the residue of the untreated blend rapidly decomposes, whereas those of the treated fabrics start to degrade at higher temperatures (see T_{max2} in Table 1) and result more stable; in addition, the treated fabrics show the highest residues at 700 °C (16.0, 19.7 and 20.9% for 5, 10 and 20BL vs. 14.7%—pure blend).

As far as silica/APP systems are concerned, silica behaves differently with respect to chitosan; indeed, such a formed architecture can act as physical barrier to the heat transfer, thus protecting the blend from thermal degradation; as a consequence, the decomposition is delayed, as evident from the $T_{onset5\%}$ values (Table 1). In spite of this, the further two decomposition steps do not change in a remarkable way (see T_{max1} and T_{max2}).

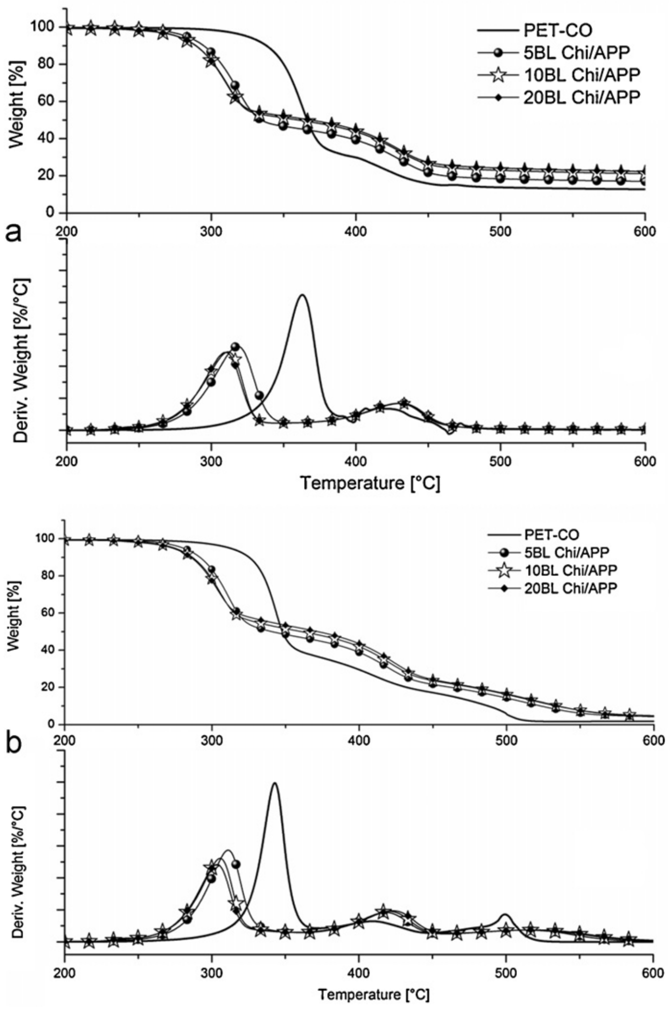

Fig. 4. TG and dTG curves of pure polyester–cotton blend and chitosan/APP-treated fabrics in nitrogen (a) and air (b).

It is worthy to note that the residues found at T_{max1} for 5 and 10BL-treated fabrics are higher with respect to the pure blend (66.7 and 63.5% for 5 and 10BL vs. 56.2%—pure blend). As a consequence, very high residues at 700 °C should be expected. On the contrary, this was not observed, probably because the formed residues were not compact and coherent and thus not thermally stable: as a matter of fact, SEM analyses pointed out the formation of several cracks within the coatings (Fig. 3c–f).

Fig. 4b plots the TG curves of the blend treated with Chi/APP in air: three decomposition peaks are shown in the corresponding dTG curves (Table 2). The first peak is attributable to cotton (343 °C), the second to polyester (407 °C) and the third (499 °C) can be related to both the fibres. Once again, the presence of chitosan anticipates the decomposition of cotton ($T_{onset5\%}$, T_{max1} and corresponding residue in Table 2) and delays the decomposition of polyester (T_{max2} and corresponding residue in Table 2). The third step, related to the intrinsic char formation of cotton and polyester, is postponed for the Chi/APP pairs, as confirmed by T_{max3} values. Furthermore, the corresponding final residues turn out to be more thermally stable than that left by the pure blend, also at 700 °C (residues at T_{max3} and at 700 °C in Table 2).

Referring to the silica/APP systems, silica is able to delay the decomposition of cotton in the blend also in air (see $T_{onset5\%}$, in Table 2), but is not able to protect the blend from the further thermo-oxidation: the variations of the weight loss rate at T_{max1}, T_{max2} and T_{max3} are almost negligible. In addition, only a slight increase of the residues at T_{max3} and at 700 °C is observable.

3.4. Flame retardancy properties

In order to describe a realistic fire scenario, it is important to test both the ignitability of a sample in the presence of a flame spread (flammability) and the combustion behaviour of the same sample under the irradiative heat flow developed as a consequence to the flame exposure. Therefore, the flame retardancy properties of the prepared samples were measured according to such two different tests.

Table 3
Flammability data.

	Burning time (s)	Afterglow time (s)	Residue (%)
PET-CO	35 ± 1	36	0
5BL Chi/APP	35 ± 1	n.o.[a]	4.5 ± 1.7
10BL Chi/APP	34 ± 4	n.o.	5.8 ± 2.0
20BL Chi/APP	34 ± 1	n.o.	7.1 ± 0.5
5BL silica/APP	39 ± 3	n.o.	2.5 ± 2.2
10BL silica/APP	38 ± 3	n.o.	3.8 ± 3.0
20BL silica/APP	40 ± 4	n.o.	7.1 ± 3.8

[a] Not observed.

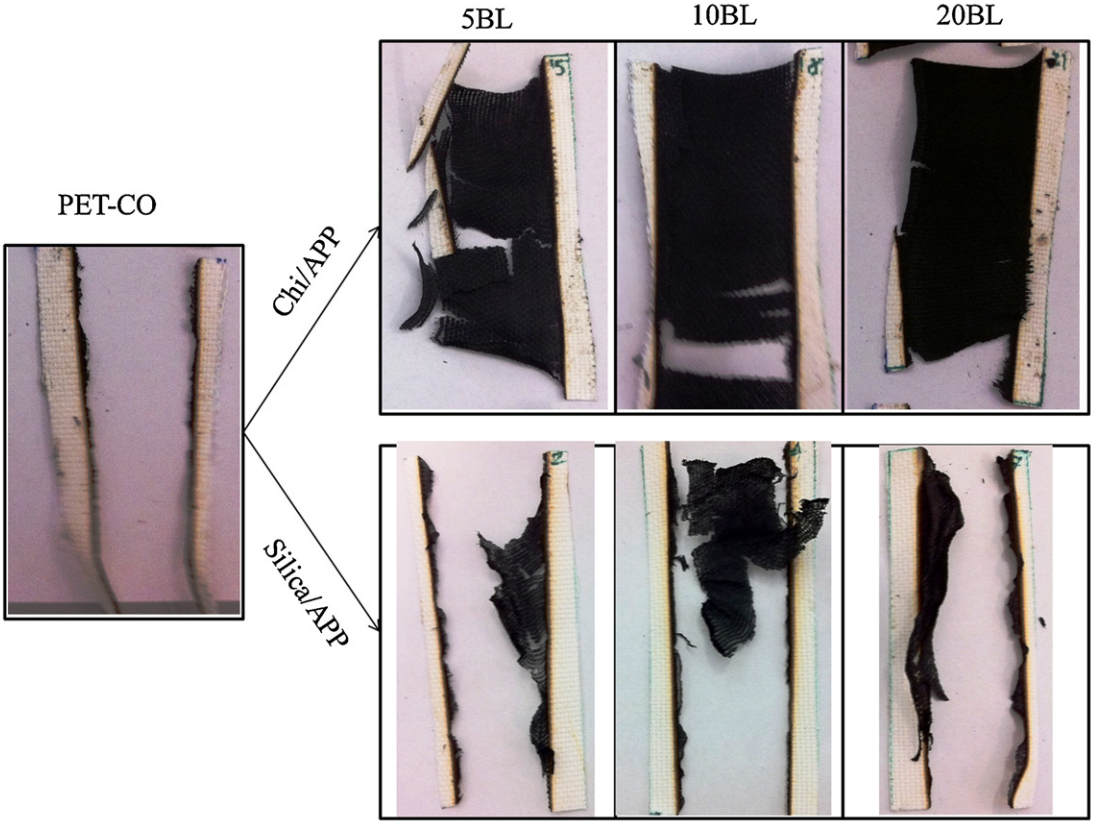

Fig. 5. Residues of pure polyester–cotton blend and chitosan/APP- and silica/APP-treated fabrics after flammability tests.

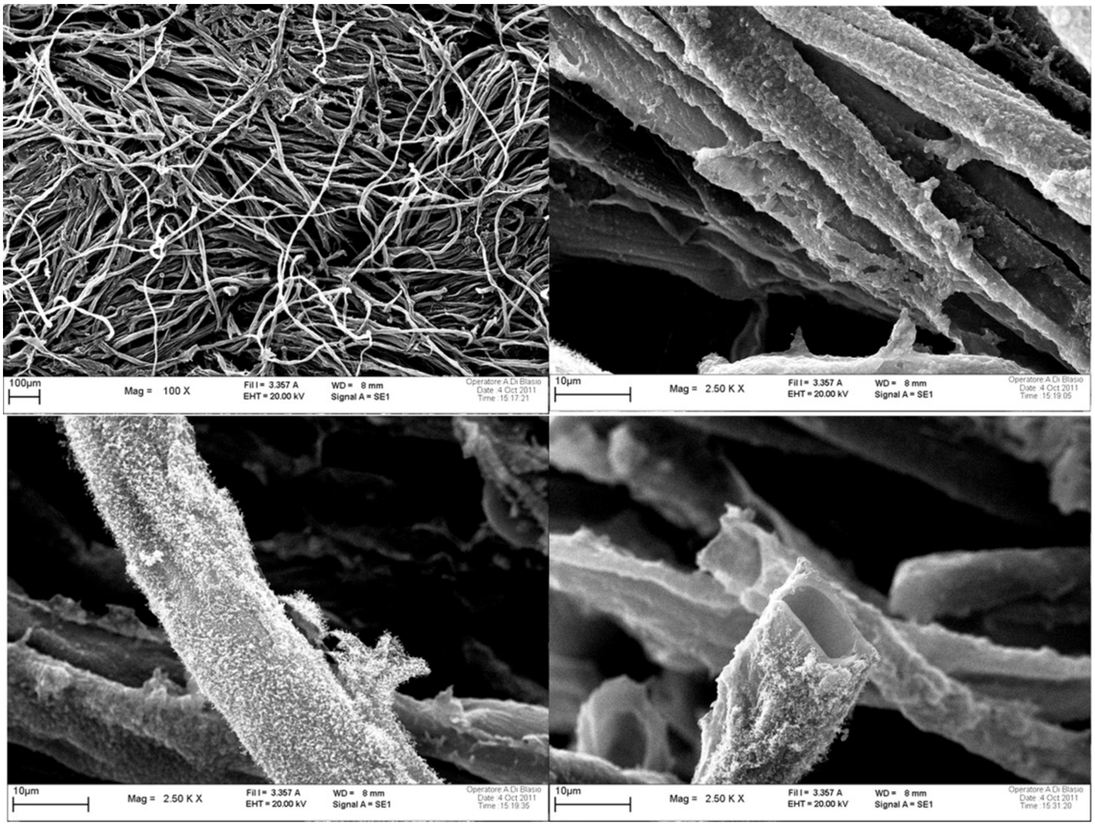

Fig. 6. SEM magnifications of the residue left by 20BL chitosan/APP-treated fabric after flammability tests.

Table 4
Cone calorimetry data.

Sample	TTI ± σ (s)	THR (MJ/m^2)	pkHRR ± σ (kW/m^2)	TSR (m^2/m^2)	SPR (m^2/s)	pkCO (ppm)	pkCO$_2$ (%)	CO$_2$/CO yield	Residue (%)
PET-CO	22 ± 2	5.0 ± 0.1	170 ± 3	45 ± 3	0.023 ± 0.004	90 ± 12	0.20 ± 0.01	42	2.6 ± 0.4
5BL Chi/APP	12 ± 3	4.7 ± 0.1	162 ± 6	54 ± 1	0.035 ± 0.010	300 ± 10	0.26 ± 0.03	17	3.4 ± 0.5
10BL Chi/APP	17 ± 6	4.1 ± 0.2	138 ± 16	56 ± 13	0.027 ± 0.007	353 ± 15	0.26 ± 0.02	16	5.0 ± 0.8
20BL Chi/APP	17 ± 4	3.9 ± 0.2	128 ± 3	57 ± 13	0.027 ± 0.001	374 ± 17	0.31 ± 0.03	15	5.9 ± 0.5
5BL silica/APP	33 ± 12	4.0 ± 0.9	178 ± 10	77 ± 20	0.027 ± 0.04	78 ± 20	0.42 ± 0.03	64	4.6 ± 1.0
10BL silica/APP	31 ± 5	4.3 ± 0.2	168 ± 8	69 ± 9	0.024 ± 0.002	81 ± 7	0.42 ± 0.03	65	5.3 ± 0.3
20BL silica/APP	31 ± 9	4.3 ± 0.4	172 ± 9	69 ± 11	0.025 ± 0.001	91 ± 13	0.43 ± 0.03	63	7.8 ± 0.4

The flammability data are collected in Table 3. From an overall point of view, it is possible to observe that the burning time of the untreated blend does not significantly change in the presence of the LbL architectures, irrespective of the considered assembly. In spite of this, it is noteworthy that after such LbL treatments the afterglow phenomenon observed for the pure blend disappears. This behaviour is very significant for a possible industrial application of these assemblies. Furthermore, both the systems are able to partially protect the blend from the combustion, as indicated by the residues found at the end of the test. A significant difference can be observed in Fig. 5 where some typical pictures of the specimens after the flammability test are collected. Chi/APP pair is capable to protect the blend better than silica/APP: indeed, a coherent residue is formed during the combustion, thus indicating that the assembly

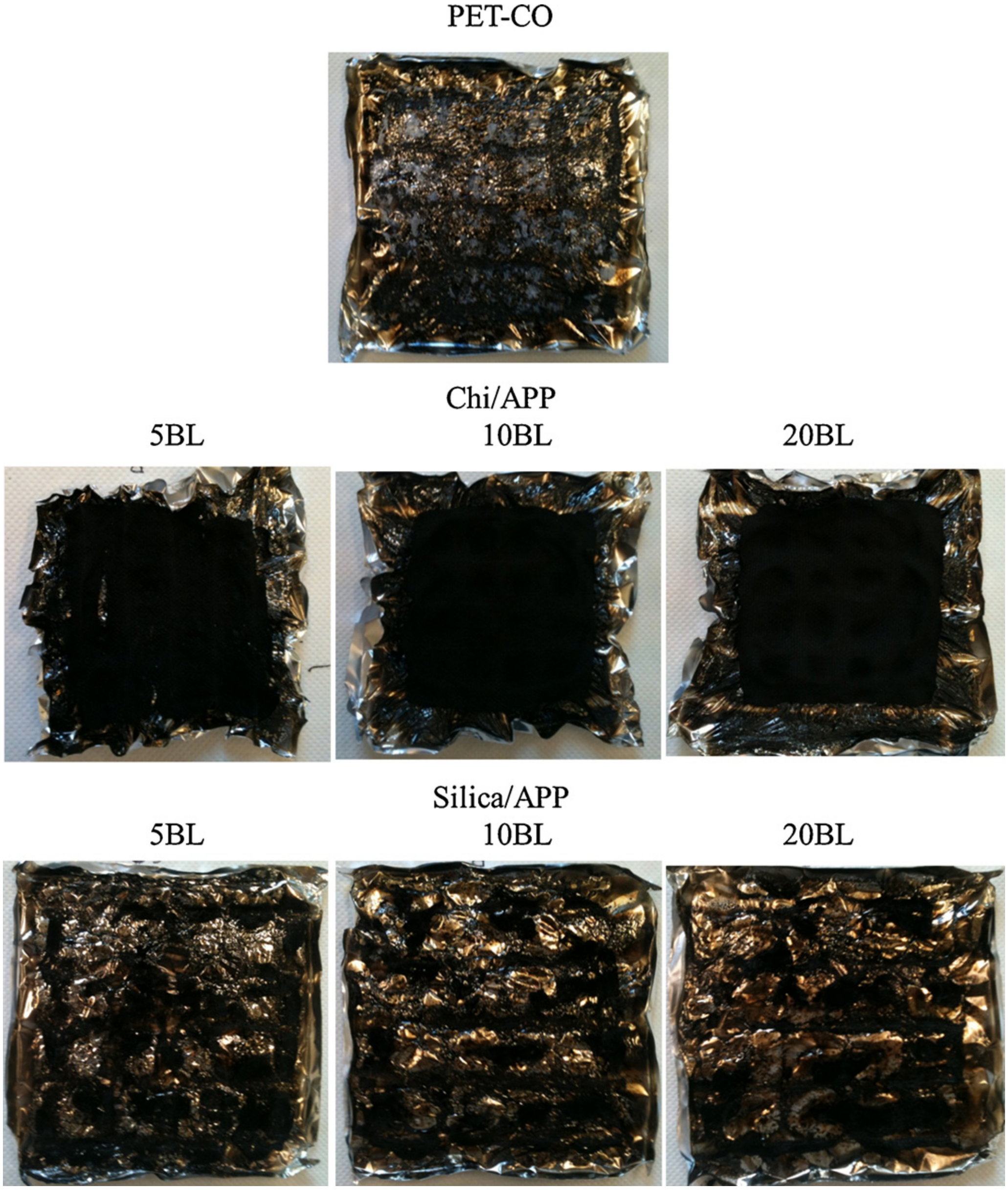

Fig. 7. Residues of pure polyester–cotton blend and chitosan/APP- and silica/APP-treated fabrics after cone calorimetry tests.

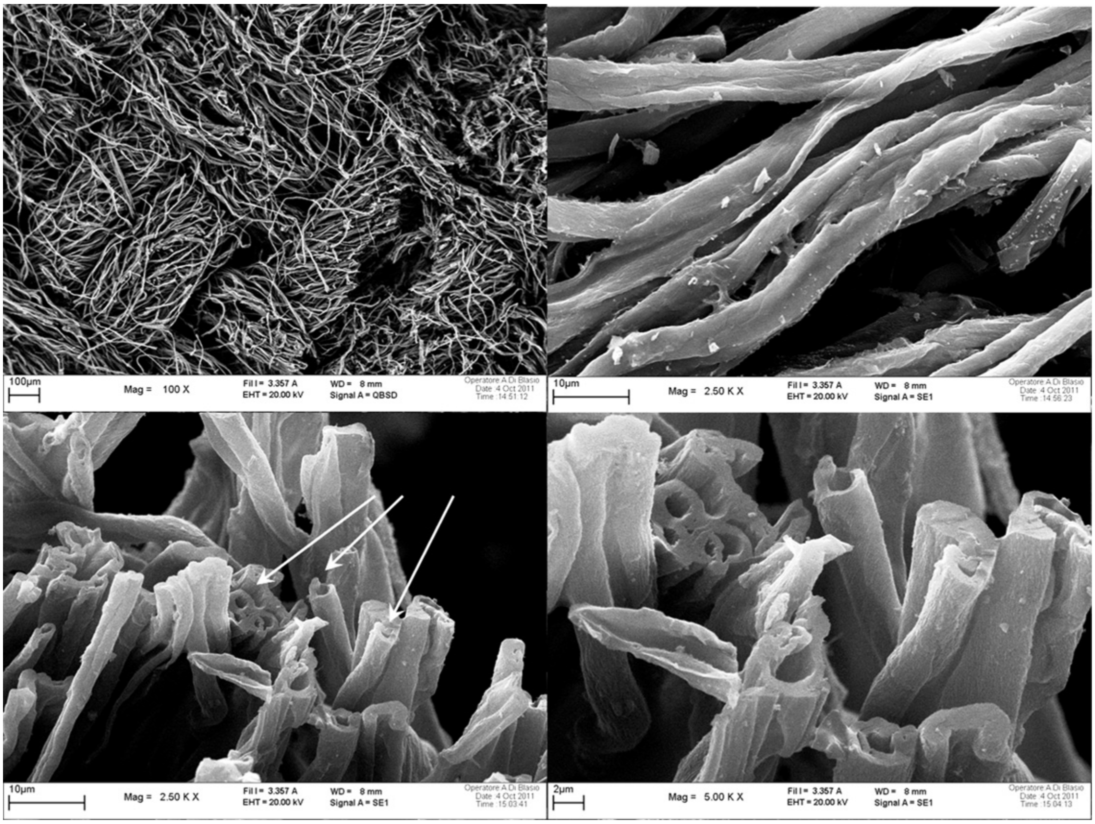

Fig. 8. SEM magnifications of the residue left by 10BL chitosan/APP-treated fabric after cone calorimeter tests.

is capable to protect the blend from the flame. SEM analyses performed on the residue show that the fabric partially maintains its original texture and hollow fibres appear after the test, as well depicted in Fig. 6 for 20BL Chi/APP-treated fabrics. On the contrary, silica/APP seems to only partially protect the blend, since it favours the carbonization of PET-CO similarly to Chi/APP system. In spite of this, the stiffness of such coatings and the presence of several cracks seem to inhibit this action mechanism. More in details, such cracks could act as preferential channels, by which the gaseous species produced during the combustion concentrate and leak, thus favouring the further combustion of the blend. This behaviour is supported by the morphological observations performed by SEM and confirms the TGA data.

The combustion behaviour of the LbL samples has been assessed by cone calorimetry: the collected data are summarized in Table 4. First of all, the time to ignition of the pure blend is anticipated by chitosan in the treated fabrics, similarly to what already observed in TG curves (12, 17 and 17 for 5 s, 10 and 20BL vs. 22 s—pure blend). As already discussed, the —OH groups can catalyse the combustion of the cotton. In spite of this, the Chi/APP pair is able to significantly reduce the total heat release and the corresponding rate (evaluated as pkHRR) in a remarkable way (162, 138 and 128 kW/m^2 for 5, 10 and 20BL vs. 170 kW/m^2—pure blend). On the basis of these results, it is possible to conclude that the higher the BL number, the lower is the combustion rate. In addition, Chi/APP turns out to be a performing flame retardant system for polyester–cotton blend because it is able to favour the char formation, slowing down the production of volatile species, as reported in Fig. 7. Furthermore, the residues at the end of the test show the formation of hollow fibres, similar to those observed after flammability tests: as an example, some typical SEM magnifications of 10BL Chi/APP-treated fabrics are depicted in Fig. 8. The most evident drawback of this system lays in the significant release of smokes (TSR) with respect to the pure blend; at the same time, the formation of carbon mono and dioxide is favoured and, interestingly, the calculated CO_2/CO ratio is lower than that for pure blend (Table 4). This behaviour confirms the occurrence of inefficient combustion due to the restricted diffusion of oxygen into the pyrolysis zone (Kandare, Kandola, Price, Nazarè, & Horrocks, 2008). Furthermore, the smoke production rate is substantially unchanged within the experimental error.

The combustion behaviour of the blend changes when chitosan is replaced with silica. This latter is able to postpone the ignition of the fabrics, as shown by the TTI values registered for the all the LBL-treated fabrics (Table 4). The THR value decreases, thus indicating that silica/APP can act as a valuable flame retardant for polyester–cotton blend since it is able to reduce the material available to burn. Nevertheless, the combustion rate does not change, since pkHRR is practically constant: once again, this finding can be probably ascribed to the morphology of such coating, which exhibits several cracks. These results confirm those observed for the flammability tests.

Referring to the smokes produced during combustion, it is possible to observe a significant increase of TSR and pkCO_2, although in this case this latter shows higher values with respect to both pure blend and Chi/APP-treated fabrics. The pkCO decreases by 12 and 10% for 5 and 10BL, respectively, while no changes are registered for 20BL. This finding suggests that a catalytic effect probably exerted by the alumina coating of silica, favours the conversion of CO to CO_2 (Table 4).

4. Conclusions

Chitosan molecules and silica nanoparticles have been coupled with ammonium polyphosphate in order to obtain two different architectures through a LbL deposition process, to be used as novel flame retardant systems. More specifically, 5, 10 and 20 bilayers were deposited on a polyester–cotton fabric blend: the LbL architectures turned out to enhance the overall flame retardancy of the fabric blend, according to their specific different action mechanisms. The most significant result concerned the suppression of the afterglow phenomenon, together with a significant increase of the residue after the test. Finally, the combustion behaviour was found to be strongly dependent on the morphology of the LbL assembly.

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