

Thermal behaviour and flame retardancy of monoethanolamine-doped sol-gel coatings of cotton fabric

Ana Marija Grancaric¹, Claudio Colleoni², Emanuela Guido², Lea Botteri¹, Giuseppe Rosace^{2,*}

¹ University of Zagreb, Faculty of Textile Technology, Prilaz baruna Filipovica 28a, HR-10000

Zagreb, Croatia

² University of Bergamo, Department of Engineering and Applied Sciences, Viale Marconi 5,

20244, Dalmine (Bg), Italy

Abstract

Recent studies have shown that the combustion behaviour of cellulose-based materials can be strongly affected by the presence of a protective phosphorus-rich silica coating obtained with a promising sol-gel approach. Thus, in the present work, monoethanolamine (MEA) was used in combination with diethylphosphatoethyltriethoxysilane sol-gel precursor (DPTES) to investigate both the ability of MEA to neutralize the acidic conditions of DPTES sol before cotton fabric treatment and the fire resistant properties of the obtained coating (COT-A). Moreover, to study the influence of an inorganic–organic silica matrix on the durability of the proposed flame retardant finishing, the DPTES-MEA sol was mixed with tetraethoxysilane (TEOS) and 3-glycidoxypropyltriethoxysilane (GPTES) precursors, to produce hybrid coatings on cotton fibres (COT-B). Scanning Electron Microscope (SEM) and Attenuated Total Reflection-Infrared (ATR-IR) spectroscopy were used to characterize the surface morphology, as well as the chemical structure of the treated and untreated fabrics. Furthermore, thermogravimetric Analysis (TGA), Microscale Combustion Calorimeter (MCC), and Limiting Oxygen Index (LOI) were performed on the treated cotton fabrics with a promising outcome. The results showed that DPTES-MEA sol is

able to enhance the thermal and thermo-oxidative stability of cotton, exploiting the joint effect of thermal shielding (exerted by the silica phases) and char-forming (exerted both by the phosphoric acid source present in the alkoxy silane precursor and by the nitrogen content in MEA). Both proposed sol-gel treatments allow the cotton samples to achieve a LOI value of 29, classifying them as self-extinguishing materials.

Keywords: Sol-gel; Fire retardancy; Thermal behaviour; Microscale Combustion Calorimeter (MCC); Limiting Oxygen Index.

1. Introduction

Even though the use of synthetic fibres has grown dramatically during the last years, cellulose based polymer is still one of the most important fibrous materials in the textile industry. This is due to its excellent intrinsic characteristics including comfort, biodegradation, hygroscopic, regeneration and softness properties. Among the natural textile fibres, cotton is one of the most important materials used to produce apparel, home furnishings and workwear but, due to its low Limiting Oxygen Index (LOI) and combustion temperature (360-425°C), this biopolymer is inflammable. Consequently, it is necessary to develop successful flame-retardant systems to prevent its fire hazards. In the last years several flame retardant finishings have been developed to comply with fire safety regulations and extend the use of cotton in textile applications requiring flame resistance. In particular, a lot of effort has been undertaken to develop flame retardant finishes containing phosphorus and nitrogen instead of halogen-containing flame retardant, as the latter releases smoke and harmful substances during combustion [1,2]. According to flame retardancy mechanism, compounds that contain phosphorous are transformed into phosphoric acid during thermal degradation or combustion. Consequently, the formed non-volatile polyphosphoric acid is able to react with the decomposing macromolecule by esterification and dehydration promoting char residue formation [3, 4]. Acting as a barrier, the char residue protects the underlying polymer

from attack by oxygen and radiant heat, thus extinguishing the fire. Advantages, such as the low release of toxic gases during combustion, can be observed using nitrogen-containing phosphorus based flame retardant compounds [5]. In fact, through the formation of a phosphorous-nitrogen intermediate, the presence of nitrogen in molecules such as dicyandiamide, melamine and urea [6] can accelerate cellulose phosphorylation, synergizing the flame retardant action of phosphorus [7]. Recently the sol-gel technique has been reported to be an encouraging and versatile approach to create transparent films on the fabric surface at room temperature. Particularly, great attention has been dedicated to the development of textile samples showing antimicrobial, antimosquito or ultraviolet radiation protection [8,9,10], dye fastness [11], anti-wrinkle finishing [12], hydrophobicity [13], biomolecule immobilization [14], self-cleaning properties [15] and sensing characteristics [16, 17]. Moreover, sol-gel technique has been shown to be able to produce a thermal shielding effect on the polymer surface, improving the flame retardancy of treated fabrics [18, 19].

As recently investigated [20, 21, 22], hybrid organic-inorganic finishes, containing both P and Si elements, can be used for textile finishing able to increase char residue during combustion and to improve thermal shield properties, due to the phosphoric-acid source and the inorganic network, respectively. To this aim, diethylphosphatoethyl-triethoxysilane (DPTES) has been employed as a precursor to synthesize hybrid organic-inorganic phosphorus-silicon coatings to enhance cotton flame retardancy. In the last years different aspects such as the use of a multi-step sol-gel process [23, 24], the presence of a condensation catalyst [24], the role of the precursor pre-hydrolysis [25] and the synergism occurring when other phosphorus or nitrogen- sources are employed [22, 26, 27, 28] have been investigated by the authors. In some cases it has been established that a synergistic effect between phosphorus and silica occurred in the realized cotton fabric finishing. In all proposed formulations the aqueous solutions obtained by DPTES precursor showed strongly acidic values. Consequently, to avoid the disadvantage of affecting cotton fibres in an excessively strong acidic range, the mixtures were partially neutralized with sodium hydroxide to obtain a slightly acidic

solution with low acid-catalyzed depolymerization of cellulose polymer. As well as other species containing available electron pairs, ethanolamines are useful in pH adjustment. Indeed, in acidic environment, they are able to accept proton onto their basic amino group, thus acting as Brønsted-Lowry bases. Particularly monoethanolamine (MEA), a small-molecular weight nitrogen-containing buffering agent, is a commonly used alkanolamine to remove sour gases (e.g. H₂S and CO₂) from natural gas during refining in the so-called “sweetening process” [29]. The present work aims to study the effect of MEA in the sol-gel preparation of DPTES flame retardant treatment for cotton fabrics. The selected molecule, composed of a polar hydroxyl group and a polar amino group joined by a two carbon alkyl chain, has been used for two reasons: first because it replaces sodium hydroxide to neutralize DPTES acidity, and second because it contributes to the nitrogen content required for additive effect with phosphorus in the flame retardant mechanism of cellulosic fabric. Considering that, at the best of our knowledge, no studies on this dual purpose have been reported so far, we decided to study the effect of MEA on the thermal behaviour of DPTES treated cotton fabrics. Moreover, to investigate the influence of an organic-inorganic silica matrix on the durability of the proposed flame retardant finishing, the DPTES-MEA sol was then mixed with a solution of 3-glycidoxypropyltriethoxysilane (GPTES) and tetraethoxysilane (TEOS), with the aim of achieving washing fastness silica coatings on the cotton fibres. The feasibility of increasing durability of sol-gel matrix onto textile fabrics using GPTES has already been demonstrated in previous studies [8, 30]. Scanning electron microscopy (SEM) and infrared (IR) spectroscopy have been exploited to investigate the surface morphology and chemical structure of thin film derived from DPTES-based xerogels applied on cotton fabrics. Thermal stability of the treated samples were then evaluated using thermogravimetric analyses (TGA) and microscale combustion calorimeter (MCC). Finally, to investigate the relationship between degradation behavior and flame retardancy of cotton samples, the degree of flame retardancy was determined by Limiting Oxygen Index (LOI), never measured in previous investigations on DPTES finishing.

2. Material and Methods

2.1. Materials

Cotton fabric (scoured and bleached plain-weave, 100% cotton, 240 g/m²) was used as substrate. The sol-gel precursors were purchased from Gelest (DPTES, 95%) and Sigma Aldrich (TEOS, 98%; GPTES, 97%) and used as received. Hydrochloric acid (HCl, 37.5%), ethanol absolute and monoethanolamine (MEA, 99%) were supplied by Sigma-Aldrich and used without any further purification. The untreated and treated cotton samples were conditioned under 65 ± 4% R. H. at 20 ± 2 °C, before all the experiments.

2.2. Nanosol preparation and application process

20.14 mL (0.06 mol) of silane precursor (DPTES) were hydrolysed with 16 mL (0.2 mol) of HCl (37.5%), in the presence of 5 mL of ethanol for 10 h under vigorous mechanical stirring and reflux conditions. Finally, distilled water was added to a total volume of 100 mL and the pH was adjusted to 5 by adding pure monoethanolamine dropwise and mixing with a magnetic stirrer. The obtained sol (Sol-A) showed a DPTES:MEA molar ratios equal to 1:3.5; according to this stoichiometry, the resultant P:N atomic ratio was set at 1:3.5 for DPTES-MEA sols.

The formulation with TEOS/GPTES (Sol-B) was produced according to a similar procedure. Initially, the DPTES solution was prepared, as previously described, mixing under mechanical stirring 20.14 ml of DPTES (60 mmol), 16 ml of HCl (37.5%) and 5 ml of ethanol. Then into the sol was added one-third of the monoethanolamine, 4.18 ml of GPTES and 3.12 ml of TEOS. The so obtained solution was stirred for 3 hours to complete the hydrolysis of both precursors. Finally, the rest of MEA and water was added to reaching a volume of 100 ml and a pH value of 5. The cotton samples (25 cm x 35 cm) were wetted with the hybrid sols and then were passed through a two-roll laboratory padding machine at nip pressure of 1.5 bars with about 80-90% of wet pick-up. After drying at 80°C for 10 min, the fabric sample was re-coated with the same sol solution, to form a second layer and then was again subjected to drying and, finally, to thermal curing at 170°C in a

laboratory oven for 4 min. The cotton fabrics treated with Sol-A and Sol-B were coded as COT-A and COT-B, respectively. After one washing cycle the same samples were coded as COT-A W and COT-B W. The amount (A, wt% owf) of coatings on the treated samples was determined using Mettler balance (10^{-4} g) as following:

$$A = \frac{W_1 - W_0}{W_0} \times 100 \quad \text{Eq. 1}$$

where W_0 and W_1 are the weight of the sample before and after the padding and thermal treatment, respectively. For each sample, an average value was determined on the basis of the three measured data, with the standard deviation always lower than $\pm 2\%$. The calculated add-on% on treated samples was 18.2% and 19.0% for COT-A and COT-B, respectively.

2.3. Characterization techniques

Thermo Avatar 370 spectrometer, equipped with an attenuated total reflection (ATR) accessory using a diamond crystal, was used to acquire FT-IR spectra. Three replicate spectra were acquired at a resolution of 4 cm^{-1} and 128 scans for each sample over a frequency range of 650 to 4000 cm^{-1} . The samples were collected at room temperature. Average spectra for treated and washed cotton samples were normalised to the band at 1315 cm^{-1} (CH_2 wagging of cellulose), which falls in a region where siloxane absorptions are not present.

Tescan Scanning Electron Microscopy/energy dispersive X-ray spectroscopy (SEM-EDX, Model MIRA\LMU), operating at 20 kV and at various magnification levels, was used to investigate the surface morphology and to carry out chemical micro-analysis. In order to increase their electrical conductivity, all analyzed samples were coated with Au/Pd.

Thermogravimetric Analysis (TGA) were carried out on PerkinElmer Model TGA Pyris1 where 5 mg of sample was stacked in an open platinum pan. The mass loss as a function of the temperature was measured in air atmosphere within the range from 50°C to 800°C and a heating rate of $30^\circ\text{C}/\text{min}$.

According to ASTM D7309-2007 (Method A), Microscale Combustion Calorimeter (MCC) measurement was performed using Govmark micro-scale combustion calorimeter Model MCC-2. A Wiley mill was used to form homogeneous powders from textile fabrics with the aim to improve sample uniformity. All fabric samples, each one approximately 5 mg, were analyzed from 50 to 600°C at the heating rate of 1.0 °C/s, in a stream of nitrogen flowing at 30 cm³/min flow rate. The sample was placed in a sample holder located on the top of the sample mounting post. The measurement of the sample cup temperature was carried out by a thermocouple passed through the center of this post with its tip at the platform on the top. The heat release combustion was determined by the oxygen depletion, since it is related to oxygen concentrations and flow rates of the gases involved in the combustion process. Each result was an average of data collected on three measurements. Limited Oxygen Index tests (LOI) were performed to study the combustion performances of treated and untreated textile samples. LOI values were measured on Dynisco limiting oxygen index chamber according to ISO 4589:1996, using fabrics strips (14 cm x 5.2 cm). To test the durability of sol-gel based films, the coated textiles were subjected to one washing cycle according to the standard EN ISO 6330:2000. TGA and LOI measurements were used to confirm the presence of the coating onto washed samples. Finally, FT-IR spectroscopy was employed to analyze the residues collected after TGA and LOI tests made on unwashed and washed samples, using the same instrument and procedure above reported.

3. Results and discussion

3.1. FT-IR analysis

To confirm the successful application of coatings onto cotton fabrics, FT-IR spectroscopy was used to characterize absorption bands corresponding to functional groups present in the molecules of sol-A or sol-B and non-existent in the pristine cotton sample (Fig. 1). First considering the untreated cotton sample spectrum, the broad band at about 3334 cm⁻¹ and the weak band at 2900 cm⁻¹ can be attributed to stretching vibration of hydroxyl groups, including hydrogen bonds, and of CH₂ and CH

groups respectively. At the same time, the characteristic peaks shown at 1053, 1315, 1369 and 1428 cm^{-1} are ascribed to the asymmetric in-plane ring stretching, C-H wagging, C-H deformation stretching and C-H in-plane bending, respectively. Regarding the treated samples spectra, the characteristic cellulose O-H stretching vibrations at 3500-3000 cm^{-1} appears as a wide, broad peak, due to the O-H stretching (3640-3160 cm^{-1}) and N-H stretching (3500-3000 cm^{-1}) of monoethanolamine [31] on the surface of the treated sample. Furthermore, the presence of MEA amino group is observed at about 1634 and 1520 cm^{-1} assigned at symmetric and asymmetric N-H bending modes, respectively.

Moreover, the IR absorption bands at 1053 cm^{-1} (Si-O stretching) and at 777 cm^{-1} (Si-O-Si symmetric stretching) suggest a Si-O-Si basic skeleton in all the treated samples, confirming the formation of the silica network. In the same spectra, the presence of a hybrid coating on treated fabrics can be confirmed by the appearance of the shoulder peak at about 1210 cm^{-1} , which is assigned to P=O absorption band, involved in the formation of hydrogen bonds with cellulose [21, 22]. Unfortunately, other vibration bands ascribable to the precursor are not easily identifiable on treated samples, since their peaks are overlapped by the IR absorption bands of cellulose.

FIGURE 1

3.2. SEM-EDX analysis

The morphological changes in the fabric surfaces induced by the application of DPTES-MEA sols onto the cotton fabrics were investigated by SEM technique and the related images for treated and untreated samples are shown in Fig. 2.

FIGURE 2

The surface of pure cotton fibres shows a normal spiral structure, characterized by a certain inhomogeneity level due to natural growth. When the fabrics are treated by sols, all the proposed finishes result in a homogeneous and compact film. The surface of treated samples become rougher than the untreated sample, due to the presence of the coating that covers the fibres completely. Energy dispersive X-ray analysis (EDX) was used to analyze the composition of the treated and

untreated textile fabrics. The experimental results, listed in Table 1, reveal that silicon, nitrogen and phosphorus are the only detectable elements in addition to the uncoated surface.

TABLE 1

3.3. Thermogravimetric analysis (TGA)

To study the thermal behaviour of materials, thermal-oxidative decomposition processes of the sol-gel treated samples have been assessed and compared with that of untreated cotton. Fig. 3a and Fig. 3b plot TG and dTG curves of the samples, while in Tables 2 thermogravimetric data are collected. As already demonstrated [33], after a mass loss at around 100°C attributed to the evaporation of trapped moisture, the pyrolysis of pure cotton in oxygen normally occurs in three steps. Initially, in the range 300-400°C, two mechanisms, producing aliphatic char and volatile products, are in competition. The first consists mainly in dehydration commencing at 210°C and ultimately resulting in a carbonaceous residue forms (char). The other, starting at about 270°C and consisting of a scission of polymer chains, is followed by formation of tars or low molecular weight products, like levoglucosan, which are much more flammable than cellulose. During the second step, at temperature of around 400 and 800°C, the simultaneous char oxidation and carbonization result in some aliphatic char that converts into an aromatic form, producing CO and CO₂. In the last step, starting from 800°C, the char and the residual hydrocarbon species are further oxidized mainly to CO and CO₂.

Compared with the above mentioned thermal behaviour of the untreated samples, the TG and dTG curves of the DPTES based sol-gel coated fabrics (Figure 3) show a large anticipation of the decomposition temperature and an increase in the char amount content at 750°C as well.

FIGURE 3

Particularly, in respect to the thermal degradation of the untreated fabric measured at 419°C, both the curves of treated samples are shifted to lower temperatures, with a first of weight loss rate at around 290°C, presumably arising from MEA decomposition, and a second at 385°C, promoted by the phosphorus contained in DPTES, supported by the additive effect of nitrogen included in

monothenolamine. In fact, as already demonstrated in our previous research [22,24,25], the occurrence of phosphorus acid, produced by the decomposition of DPTES at a lower temperature than cotton, catalyzes cellulose dehydration as a char-promoter in the condensed phase. This behaviour facilitates carbonaceous residue formation, stabilizes the structure of the treated cotton sample, giving less volatile and nonflammable components. These performances are enhanced by the presence of MEA, as a source of nitrogen, used in this work to neutralize the strong acidic value of pure DPTES, to provide a synergistic effect with phosphorous and to dilute the volatile products of the polymer decomposition as well. At the same time, the inorganic nature of the silica network is able to shield the cellulose, stabilizing the char against the oxidation process thus producing a higher amount of char when compared to the untreated cotton sample. In fact, as confirmed by the residues at T_{max} listed in Table 2, the char left by the sol-gel treated samples is much higher (58.7% and 60.0% for COT-A and COT B, respectively) than that of pure cotton (37.5%). Then, upon reaching 600°C, the carbonaceous structures derived from the pure cotton decomposition begin to be thermally stable with a char residue lower than 1%, while a significant amount of residue is still observed for the samples treated with Sol-A and Sol-B (28% and 32% respectively). This significant increase in the char yield is in agreement with the flame retardancy effect of coatings [34], measurable at around 750°C in the reduction of weight loss from 99.5% (untreated cotton) to 90.7% (COT-A) and to 86.5% (COT-B). The higher residue for COT-B (13.5%) than that obtained using only MEA as an additive of DPTES (COT-A = 9.3%) is probably due to the presence of both TEOS and GPTES precursors that, increasing the silica content in the coating able to inhibit the oxidation of the cellulose material, improves the thermal stability of the sample. Therefore from these results it is demonstrated that the proposed finishings are able to protect cotton fabric from its thermal degradation.

TABLE 2

3.4. Microscale Combustion Calorimeter (MCC)

In order to investigate the char forming effect of the sol-gel coatings, the combustion behaviours of the fabric samples were monitored by Microscale Combustion Calorimeter (MCC) and the heat release rate (HRR) curves of control and treated fabrics are reported in Fig. 4. Heat release combustion (HRC), temperature at the maximum pyrolysis rate (T_{max}) and total heat release (THR) were determined as flammability parameters and the results are shown in Table 3. These data are very important because they reflect the combustion behaviour of textile fabrics, giving a reasonable assessment of flame hazard by small amount of samples.

FIGURE 4

TABLE 3

The HRR versus temperature curve indicates that the untreated cotton starts to decompose and to form fuel gases at less than 300°C, and presents the peak heat release rate (pHRR= 235 W/g) at about 384°C (T_p) with an estimated value of about 12 kJ/g in THR. Regarding the treated samples, a significant reduction in THR, pHRR, HRC and T_{max} and an increase in the char yield are noted when the cotton fabrics were treated with flame retardant coatings. Moreover, a “shoulder” appears at about 250°C for sol-gel treated fabrics, as an early peak well known empirically for cellulose-based fabric finished with flame retardants [35]. It is mainly due to the process of dehydration and decomposition of cotton induced by the phosphoric acid released at about 250°C. After that, a second peak was observed between 345-348°C showing a reduction in the normal thermal degradation of treated samples. HRC values of these peaks slightly decrease with increasing add-on values due to the presence of GPTES/TEOS silica precursors in addition to the component present in the COT-A sample, suggesting that the char forming effect increases with the growth of silica content. As a consequence of the catalyzed thermal degradation of cotton fabric, the samples drastically reduce the values of pHRR from 253.7 W/g (pure cotton) to 78 W/g and to 76 W/g for COT-A and COT-B, respectively. At the same time, Total Heat Release (THR) of all treated samples exhibits a strong reduction of more than 50% in the values respect to the pure cotton (see Table 3) thanks to the char formation, promoted by the presence of phosphorus/silica coatings, able

to protect the fabrics from further combustion. Moreover, the flame retardant performance exhibited by the combination of DPTES with monoethanolamine and silica precursors seems to be approximately the same of DPTES-MEA finishing. Both of the sol-gel finishings can efficiently reduce the heat feeding back to the cotton surface due to the insulating effect of silica coatings, as well as the degradation temperature thanks to the P and N content, in agreement with the TG analysis.

3.5. Limiting Oxygen Index (LOI)

By Limiting Oxygen Index (LOI) values it is possible to demonstrate both the ability of a textile fabric to ignite and the flame retardant level of treated samples. Since air is composed of approximately 21% oxygen by volume, textiles with an LOI of less than this value burn easily in this atmosphere. In this way, materials in the range from 21 to 27.9 vol% will rank as slow burning, while above this range they are classified as self-extinguishing [36, 37]. Consequently, with a LOI of $\approx 18\%$, pure cotton is among the most flammable textile fibres [38]. The results, obtained from LOI testing of treated and untreated samples, are summarized in Table 4.

TABLE 4

When DPTES sols are combined with MEA or MEA and silica precursors, a clear flame-retardant effect can be recognized on the two treated samples respect to the pure cotton both by drastically increasing LOI values and by decreasing burning time. Particularly, both treatments exhibit a LOI index of 29, which allows a classification of the treated samples as self-extinguishing fabrics.

As demonstrated by Lyon et al. [39], using the data collected by MCC, it is possible to correlate the results with the thermal combustion properties, predicting the minimum oxygen concentration that will support flaming combustion of textile fabrics. According to the above mentioned authors, a physical model for the LOI test was used as shown in Eq. (2).

$$LOI = OI + \frac{\sigma T_{PHRR}^4}{a} + \frac{HRR * \eta_g / a \chi^2}{(1 - \mu)^2 HRC} \quad \text{Eq. 2}$$

where, OI is the lowest oxygen volume fraction for combustion of gaseous fuels at the lower flammability limit, σ is the Boltzmann radiation constant, T_{PHRR} is the temperature at peak heat release rate in the MCC, a is the proportionality constant between flame heat flux and the oxygen concentration in the atmosphere, HRR^* is the critical heat release rate at ignition/extinction, $\eta_g = Lg/\Delta Tp \approx 2 \text{ kJ/g}/50 \text{ K} = 40 \text{ J/g-K}$ is the heat absorption capacity expressed as the heat of gasification Lg and the pyrolysis temperature interval ΔTp in the MCC, χ is the combustion efficiency of the fuel gases in ventilated flaming combustion, μ is the inert fraction and HRC is the heat release capacity in the MCC [38]. In Eq. (2), three separate contributions are clearly shown. The first term is referred to the gas phase (OI), the second to the condensed phase with σT_{PHRR}^4 the ignition resistance, and the last contribution is the resistance to burning of a solid sample. Many papers [38,40] reported the parameter values as following: $OI \approx 13.5\%$, $a = 2.5 \text{ kW/m}^2\text{-}\%O_2$, $\eta_g = 2 \text{ kJ/g}/50 \text{ K} = 40 \text{ J/g-K}$, $HRR^* \approx 20 \text{ kW/m}^2$ and $\chi = 1$.

Exploiting these parameter values in Eq. (2), in combination with those of thermal combustion properties (HRC , μ and $TPHRR$) obtained in this work from Microscale Combustion Calorimeter, the LOI of the tested textile samples was calculated. The results reported in Table 4 clearly show a reasonable agreement between measured and calculated values of LOI (%) for treated and untreated samples.

3.6. FT-IR analysis of char residues

Considering that the chemical structure of the charred layer plays a significant role in the performance of a flame retardant, FT-IR spectroscopy analysis was carried out to investigate the char structures of pyrolyzed fabrics and to determine the mechanism by which they are formed. For this reason, the residue left after TGA experiments were collected and subjected to FT-IR analysis and the results are displayed in Fig. 5.

FIGURE 5

Respect to the unpyrolysed fabrics, in the COT-A and COT-B residue samples a decrease in the intensity of the absorption bands between 3640-3160 cm^{-1} and around 2900 cm^{-1} was observed. These peaks, assigned to O-H and C-H bond stretching vibrations, indicates high efficient dehydration and cross-linking reactions during combustion. At the same time, the absorption band at around 1578 cm^{-1} suggests the formation of rich C=C structures as well as aromatic compounds. Moreover, the peaks around 1060 and 790 cm^{-1} assigned to Si-O-Si stretching mode and Si-O-Si bending vibration, respectively, confirm the presence of the inorganic SiO_2 matrix in all the charred residues. These results show that, upon heating, flame retardant finishing reacts with cellulose and acts as char-promoter, contributing to the thermal shield effect of the coating. The presence of a certain amount of char means that hybrid finishings have favored the formation of aromatic species, inhibiting that of the hydrocarbon counterparts.

3.7. Durability tests

In order to evaluate the washing fastness of the flame retardant coatings, TGA, MCC and LOI tests were performed on treated samples submitted to a washing cycle. It can be seen that, respect to the untreated cellulose, the TG curves of the washed COT-A and COT-B samples show analogous shape and the same anticipation of the thermal degradation observed for unwashed treated fabrics (Fig. 6). At the same time, the weight loss at around 290°C, observed in the unwashed samples and assigned to the decomposition of MEA, completely disappears confirming the leaching of monoethanolamine from the treated samples after one washing cycle. The data shows that the char yield at 600°C, almost null for the untreated cotton sample, decreases from 25-30% to 12-15% after the washing cycle for both the coated samples. Finally, above 700°C, the treated cotton fabrics show no complete volatilization in air atmosphere and 3% of solid residue remains for COT-B, suggesting that a low amount of silica film is still present on the coated fabrics after one washing cycle. This phenomenon can be related to the presence of GPTES/TEOS in combination with

DPTES-MEA able to increase the immobilization of Sol-B onto cotton fabrics so much so that its char residue is around 40% greater than those obtained with Sol-A.

FIGURE 6

The heat release rate curves of the untreated and treated cotton fabrics, these latter subjected to one home laundering cycle, are presented against the heating temperature in Fig. 7. Compared with the MCC data of COT-A and COT-B before washing (Fig. 4), it can be seen that HRR values of the washed treated samples increase, probably due to the leaching of coatings from treated samples. Moreover, from Table 3 and Table 5 it is possible to observe that the initial decomposition temperatures increase from about 170°C to 270°C, while the peak assigned to MEA decomposition (at $T_{\max 1}$) disappears completely.

TABLE 5

Nevertheless, the T_{PHHR} values at $T_{\max 2}$ show only a slight shift of about 3°C after washing and they are about 30°C far from the results observed for untreated samples (383.9°C). At the same time the THR and HRC values increase and become approximately twice the unwashed samples. Therefore, the data presented in Table 6 persuasively prove that during laundering DPTES is more resistant to hydrolysis than MEA.

TABLE 6

The different hydrolysis-resistance of two components on cotton can be attributed to the fact that silica matrix of DPTES is highly interconnected with the polar chain structure of cellulose, whereas MEA is not able to be immobilized on the fibre. These results show that the flame retardant performance of the coated textile fabrics after one washing cycle is strongly reduced even if the char yield is still considerable for the sample treated with Sol-B (about 22%). This confirms the role of the hybrid silica network in the durability of the coating.

FIGURE 7

The reduction in the flame retardant performances of coated samples was also confirmed by LOI analysis so that 20% and 21% were measured for COT-A and COT-B, respectively (Table 4). The

self-extinguish classification assigned for the LOI values of both unwashed samples decreased dramatically, meaning that the protection against combustion was reduced most likely due to the removal of MEA, and partially of DPTES, during the washing process. The presence of silica precursors in order to improve the durability of DPTES-MEA finishing show some ability to increase linkages between DPTES and cellulose. Unfortunately, it is insufficient to immobilize MEA onto cotton samples.

4. Conclusion

In the present work, environmentally friendly halogen-free flame retardant coatings were successfully realized on cotton fabric by sol-gel technique. DPTES precursor was hydrolyzed and then combined with both MEA and a mix of TEOS/GPTES precursors in order to enhance the thermal and fire stability of treated samples respect to the untreated cellulose based fabric. In particular, MEA was used with a dual-purpose: (a) to partially neutralize the acidity of the DPTES, otherwise not usable in the cotton fabric treatment, and (b) to contribute to the flame retardant effect of phosphorus-doped silica coating. At the same time, a mix of TEOS and GPTES was tested in combination with DPTES-MEA sol, both to improve the amount of silica in the textile finishing and to promote a greater immobilization of the hybrid network on the cotton surface with the aim of increasing its durability after washing cycle. The results collected by thermogravimetry, microscale combustion calorimetry and limiting oxygen index tests can be summarised as follows:

- DPTES-MEA sol is able to enhance the thermal and thermo-oxidative stability of cotton, exploiting the joint effect of thermal shielding (exerted by silica phases) and char-forming (exerted both by the phosphoric acid source present in the alkoxy silane precursor and by nitrogen content in MEA);
- SEM micrographs show that treated fabrics form a homogeneous protective layer, which increases the flame retardancy of fabric samples;

- both proposed sols allow the treated cotton samples to achieve a LOI value of 29, classifying them as self-extinguishing materials;

- after one washing cycle the residue at 800°C for COT-B is about twice the DPTES-MEA sample.

It means that TEOS-GPTES sol promotes, in some way, the immobilization of molecules onto cotton fabrics. Nevertheless its LOI value decreases dramatically from 29 to 21, showing that further studies have to be carried out to improve the durability of the proposed coatings.

Acknowledgements

The authors would like to thank European COST Action “Sustainable flame retardancy for textiles and related materials based on nanoparticles substituting conventional chemicals” FLARETEX (MP1105).

References

- [1] A.R. Horrocks, Developments in flame retardants for heat and fire resistant textiles—the role of char formation and intumescence, *Polym. Degrad. Stab.* 54 (1996) 143–154. doi:10.1016/S0141-3910(96)00038-9.
- [2] R. Grümping, M. Opel, M. Petersen, Brominated Dioxins And Brominated Flame Retardants In Irish Cow`S Milk, *Organohalogen Compd.* 69 (2007) 912–915.
- [3] K. Kishore, K. Mohandas, Action of phosphorus compounds on fire-retardancy of cellulosic materials: A review, *Fire Mater.* 6 (1982) 54–58. doi:10.1002/fam.810060203.
- [4] R. Hidersinn, *Encyclopedia of Polymer Science and Technology*, in: John Wiley & Sons, Inc., Hoboken, NJ, USA, 1977: p. 270. doi:10.1002/0471440264.
- [5] H. Horacek, R. Grabner, Advantages of flame retardants based on nitrogen compounds, *Polym. Degrad. Stab.* 54 (1996) 205–215. doi:10.1016/S0141-3910(96)00045-6.
- [6] J. Alongi, G. Brancatelli, G. Rosace, Thermal properties and combustion behavior of POSS- and bohemite-finished cotton fabrics, *J. Appl. Polym. Sci.* 123 (2012) 426–436. doi:10.1002/app.34476.
- [7] S. Chang, B. Condon, E. Graves, M. Uchimiya, C. Fortier, M. Easson, et al., Flame retardant properties of triazine phosphonates derivative with cotton fabric, *Fibres Polym.* 12 (2011) 334–339. doi:10.1007/s12221-011-0334-7.
- [8] R. Poli, C. Colleoni, A. Calvimontes, H. Polášková, V. Dutschk, G. Rosace, Innovative sol-gel route in neutral hydroalcoholic condition to obtain antibacterial cotton finishing by zinc precursor, *J. Sol-Gel Sci. Technol.* 74 (2015) 151–160. doi:10.1007/s10971-014-3589-9.
- [9] M. Ardanuy, M. Faccini, D. Amantia, L. Aubouy, G. Borja, Preparation of durable insecticide cotton fabrics through sol-gel treatment with permethrin, *Surf. Coatings Technol.* 239 (2014) 132–137. doi:10.1016/j.surfcoat.2013.11.031.
- [10] B. Mahltig, T. Textor, *Nanosols and textiles*, World Scientific, Singapore, 2008.
- [11] B. Mahltig, T. Textor, Combination of silica sol and dyes on textiles, *J. Sol-Gel Sci. Technol.*

- 39 (2006) 111–118. doi:10.1007/s10971-006-7744-9.
- [12] K.S. Huang, Y.H. Nien, K.C. Hsiao, Y.S. Chang, Application of DMEU/SiO₂ gel solution in the antiwrinkle finishing of cotton fabrics, *J. Appl. Polym. Sci.* 102 (2006) 4136–4143. doi:10.1002/app.24246.
- [13] C. Colleoni, E. Guido, V. Migani, G. Rosace, Hydrophobic behaviour of non-fluorinated sol-gel based cotton and polyester fabric coatings, *J. Ind. Text.* 44 (2015) 815–834. doi:10.1177/1528083713516664.
- [14] F.Y. Li, Y.J. Xing, X. Ding, Immobilization of papain on cotton fabric by sol-gel method, *Enzyme Microb. Technol.* 40 (2007) 1692–1697. doi:10.1016/j.enzmictec.2006.09.007.
- [15] C. Colleoni, M.R. Massafra, G. Rosace, Photocatalytic properties and optical characterization of cotton fabric coated via sol-gel with non-crystalline TiO₂ modified with poly(ethylene glycol), *Surf. Coatings Technol.* 207 (2012) 79–88. doi:10.1016/j.surfcoat.2012.06.003.
- [16] L. Van Der Schueren, K. De Clerck, G. Brancatelli, G. Rosace, E. Van Damme, W. De Vos, Novel cellulose and polyamide halochromic textile sensors based on the encapsulation of Methyl Red into a sol-gel matrix, *Sensors Actuators, B Chem.* 162 (2012) 27–34. doi:10.1016/j.snb.2011.11.077.
- [17] M. Caldara, C. Colleoni, E. Guido, V. Re, G. Rosace, Development of a textile-optoelectronic pH meter based on hybrid xerogel doped with Methyl Red, *Sensors Actuators, B Chem.* 171-172 (2012) 1013–1021. doi:10.1016/j.snb.2012.06.024.
- [18] J. Vasiljević, S. Hadžić, I. Jerman, L. Černe, B. Tomšič, J. Medved, M. Godec, B. Orel, B. Simončič, Study of flame-retardant finishing of cellulose fibers: Organic-inorganic hybrid versus conventional organophosphonate, *Polym. Degrad. Stab.* 98 (2013) 2602-2608. doi:10.1016/j.polymdegradstab.2013.09.020.
- [19] G. Rosace, R. Canton, C. Colleoni, Plasma enhanced CVD of SiO_xC_yH_z thin film on different textile fabrics: Influence of exposure time on the abrasion resistance and mechanical properties, *Appl. Surf. Sci.* 256 (2010) 2509–2516.

doi:10.1016/j.apsusc.2009.10.097.

- [20] R.S. Kappes, T. Urbainczyk, U. Artz, T. Textor, J. S. Gutmann, Flame retardants based on amino silanes and phenylphosphonic acid, *Polym. Degrad. Stab.* 129 (2016) 168–179. doi: 10.1016/j.polymdegradstab.2016.04.012
- [21] G. Brancatelli, C. Colleoni, M.R. Massafra, G. Rosace, Effect of hybrid phosphorus-doped silica thin films produced by sol-gel method on the thermal behavior of cotton fabrics, *Polym. Degrad. Stab.* 96 (2011) 483–490. doi:10.1016/j.polymdegradstab.2011.01.013.
- [22] J. Alongi, C. Colleoni, G. Rosace, G. Malucelli, Thermal and fire stability of cotton fabrics coated with hybrid phosphorus-doped silica films, *J. Therm. Anal. Calorim.* 110 (2012) 1207–1216. doi:10.1007/s10973-011-2142-0.
- [23] C. Colleoni, I. Donelli, G. Freddi, E. Guido, V. Migani, G. Rosace, A novel sol-gel multi-layer approach for cotton fabric finishing by tetraethoxysilane precursor, *Surf. Coatings Technol.* 235 (2013) 192–203. doi:10.1016/j.surfcoat.2013.07.033.
- [24] J. Alongi, C. Colleoni, G. Malucelli, G. Rosace, Hybrid phosphorus-doped silica architectures derived from a multistep sol-gel process for improving thermal stability and flame retardancy of cotton fabrics, *Polym. Degrad. Stab.* 97 (2012) 1334–1344. doi:10.1016/j.polymdegradstab.2012.05.030.
- [25] J. Alongi, C. Colleoni, G. Rosace, G. Malucelli, The role of pre-hydrolysis on multi step sol-gel processes for enhancing the flame retardancy of cotton, *Cellulose.* 20 (2013) 525–535. doi:10.1007/s10570-012-9806-1.
- [26] A.M. Grancaric, L. Botteri, J. Alongi, G. Malucelli, Synergistic effects occurring between water glasses and urea/ammonium dihydrogen phosphate pair for enhancing the flame retardancy of cotton, *Cellulose.* 22 (2015) 2825–2835. doi:10.1007/s10570-015-0671-6.
- [27] J. Alongi, C. Colleoni, G. Rosace, G. Malucelli, Phosphorus- and nitrogen-doped silica coatings for enhancing the flame retardancy of cotton: Synergisms or additive effects?, *Polym. Degrad. Stab.* 98 (2013) 579–589. doi:10.1016/j.polymdegradstab.2012.11.017.

- [28] J. Alongi, C. Colleoni, G. Rosace, G. Malucelli, Sol-gel derived architectures for enhancing cotton flame retardancy: Effect of pure and phosphorus-doped silica phases, *Polym. Degrad. Stab.* 99 (2014) 92–98. doi:10.1016/j.polymdegradstab.2013.11.020.
- [29] D.J. Kim, Y. Lim, D. Cho, I.H. Rhee, Biodegradation of monoethanolamine in aerobic and anoxic conditions, *Korean J. Chem. Eng.* 27 (2010) 1521–1526. doi:10.1007/s11814-010-0285-5.
- [30] C.X. Wang, S.L. Chen, Surface treatment of cotton using β -cyclodextrins sol-gel method, *Appl. Surf. Sci.* 252 (2006) 6348–6352. doi:10.1016/j.apsusc.2005.09.016.
- [31] A. Mushtaq, H. Bin Mukhtar, A.M. Shariff, FT-IR study of enhanced polymeric blend membrane with amines, *Res. J. Appl. Sci. Eng. Technol.* 7 (2014) 1811–1820.
- [32] P. Wakelyn, N. Bertoniere, A. French, D. Thibodeaux, B. Triplett, M.-A. Rousselle, et al., Cotton Fibres, in: L. Menachem (Ed.), *Cit. Inf. Handb. Fiber Chem.*, Third, CRC, 2006. doi:10.1201/9781420015270.ch9.
- [33] D. Price, A. R. Horrocks, M. Akalin, A. A. Farooq, Influence of flame retardants on the mechanism of pyrolysis of cotton (cellulose) fabrics in air, *J. Anal. Appl. Pyrolysis.* 40-41 (1997) 511–524. doi:10.1016/S0165-2370(97)00043-0.
- [34] A.R. Horrocks, B. Kandola, Fire Retardancy of Polymers: the Use of Intumescence, in: M. Le Bras, S. Bourbigot, G. Camino, R. Delobel (Eds.), *Fire Retard. Polym. Use Intumescence*, first, Woodhead Publishing, 1998: pp. 343–362.
- [35] T.M. Nguyen, S. Chang, B. Condon, R. Slopek, E. Graves, M. Yoshioka-Tarver, Structural effect of phosphoramidate derivatives on the thermal and flame retardant behaviors of treated cotton cellulose, *Ind. Eng. Chem. Res.* 52 (2013) 4715–4724. doi:10.1021/ie400180f.
- [36] X. Li, H. Chen, W. Wang, Y. Liu, P. Zhao, Synthesis of a formaldehyde-free phosphorus-nitrogen flame retardant with multiple reactive groups and its application in cotton fabrics, *Polym. Degrad. Stab.* 120 (2015) 193–202. doi:10.1016/j.polymdegradstab.2015.07.003.
- [37] P. Bajaj, Heat and flame protection, in: *Handb. Tech. Text.*, Elsevier, 2000: pp. 223–263.

doi:10.1533/9781855738966.223.

- [38] C.Q. Yang, Q. He, R.E. Lyon, Y. Hu, Investigation of the flammability of different textile fabrics using micro-scale combustion calorimetry, *Polym. Degrad. Stab.* 95 (2010) 108–115. doi:10.1016/j.polymdegradstab.2009.11.047.
- [39] R.E. Lyon, R.N. Walters, S.I. Stoliarov, Thermal analysis of flammability, *J. Therm. Anal. Calorim.* 89 (2007) 441–448. doi:10.1007/s10973-006-8257-z.
- [40] C.Q. Yang, Q. He, Applications of micro-scale combustion calorimetry to the studies of cotton and nylon fabrics treated with organophosphorus flame retardants, *J. Anal. Appl. Pyrolysis.* 91 (2011) 125–133. doi:10.1016/j.jaap.2011.01.012.

Figure captions

Fig. 1. FT-IR spectra of untreated (UT) and sol-gel treated cotton fabrics (COT-A and COT-B samples).

Fig. 2. SEM images of untreated (UT) and sol-gel treated cotton fabrics (COT-A and COT-B samples).

Fig. 3. TGA and dTG curves of untreated (UT) and sol-gel treated cotton fabrics (COT-A and COT-B samples) in air atmosphere.

Fig. 4. MCC curves of untreated (UT) and FR treated cotton fabrics (COT-A and COT-B samples).

Fig. 5. FT-IR spectra of char residues of the treated samples, before (COT-A and COT-B) and after one washing cycle (COT-A W, COT-B W).

Fig. 6. TGA and dTG curves of untreated (UT) and treated samples after one washing cycle (COT-A W and COT-B W samples) in air atmosphere.

Fig. 7. MCC curves of untreated (UT) and fire-retardant treated cotton samples after one washing cycle (COT-AW and COT-BW samples).

Figure 1

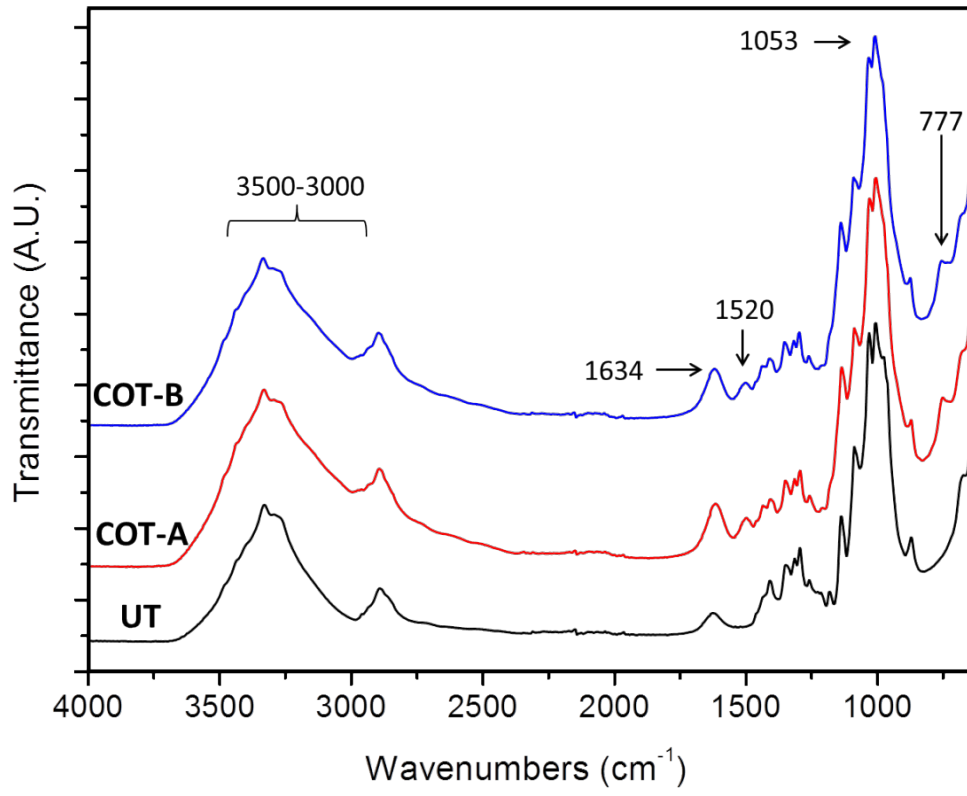
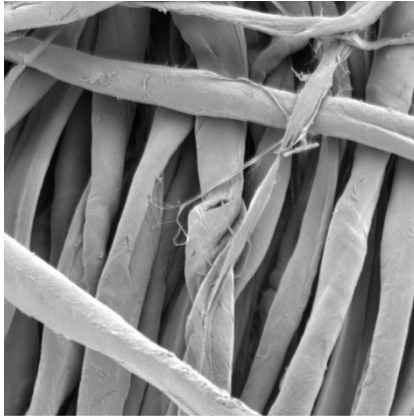
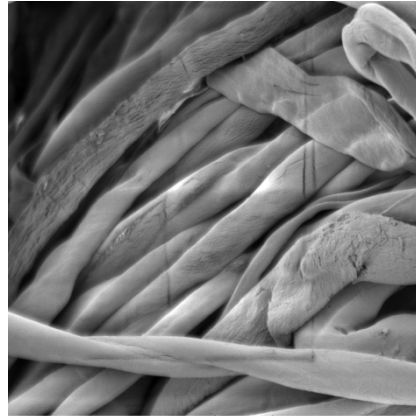


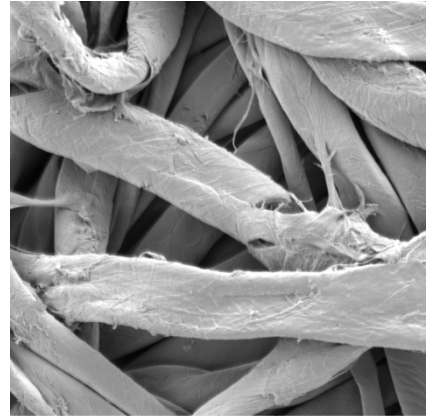
Figure 2



UT



COT-A



COT-B

Figure 3

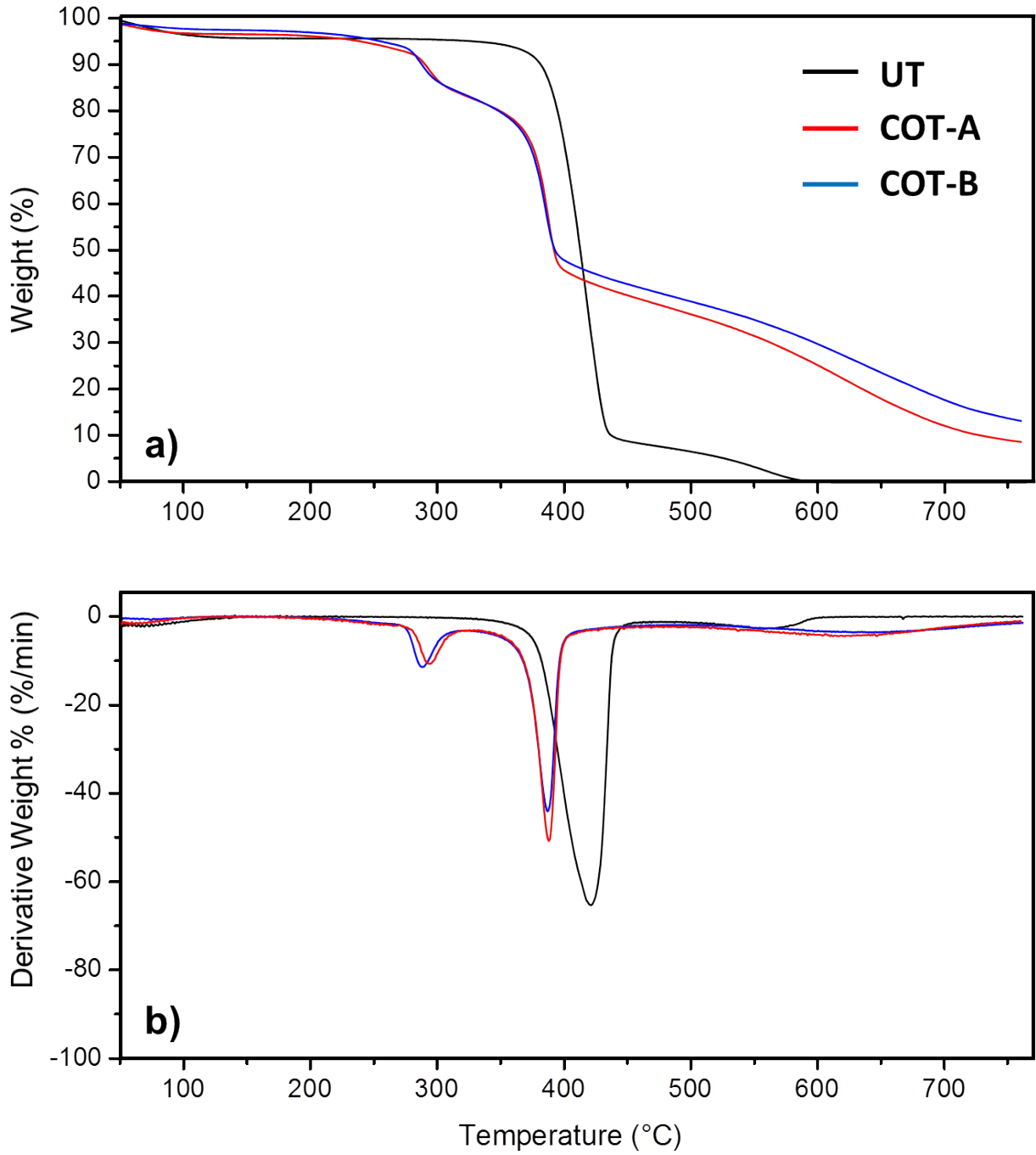


Figure 4

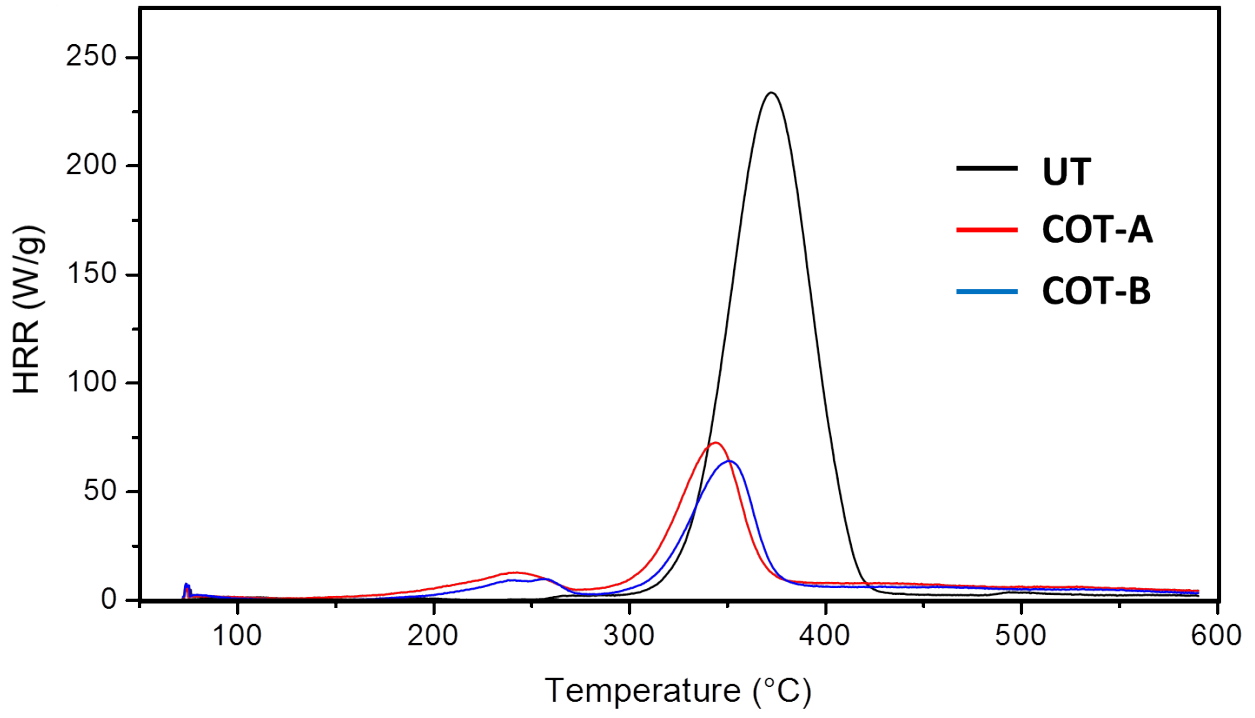


Figure 5

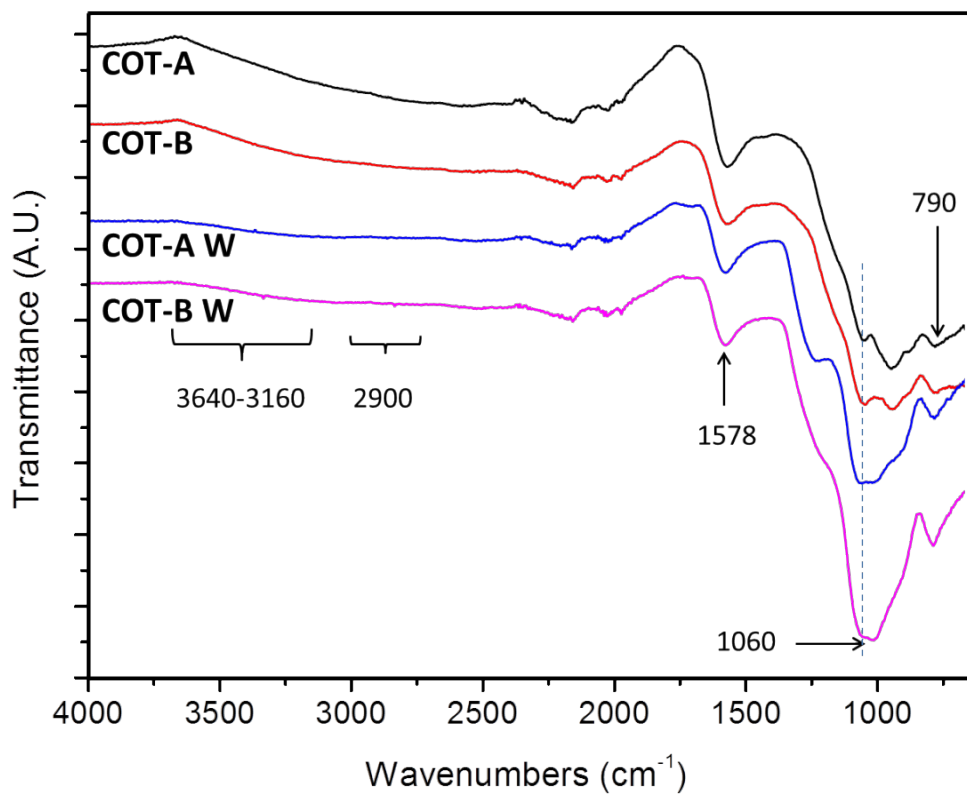


Figure 6

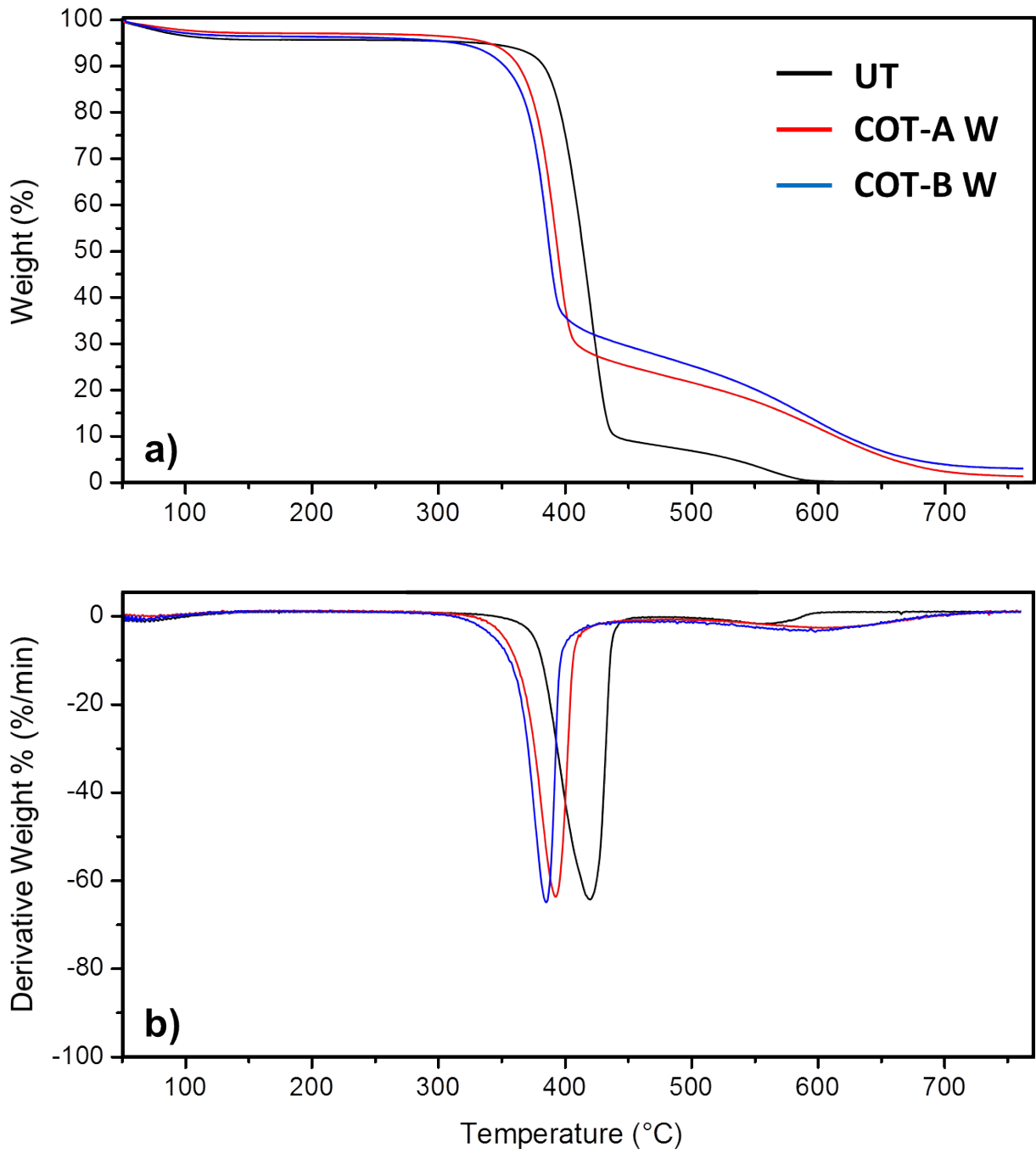


Figure 7

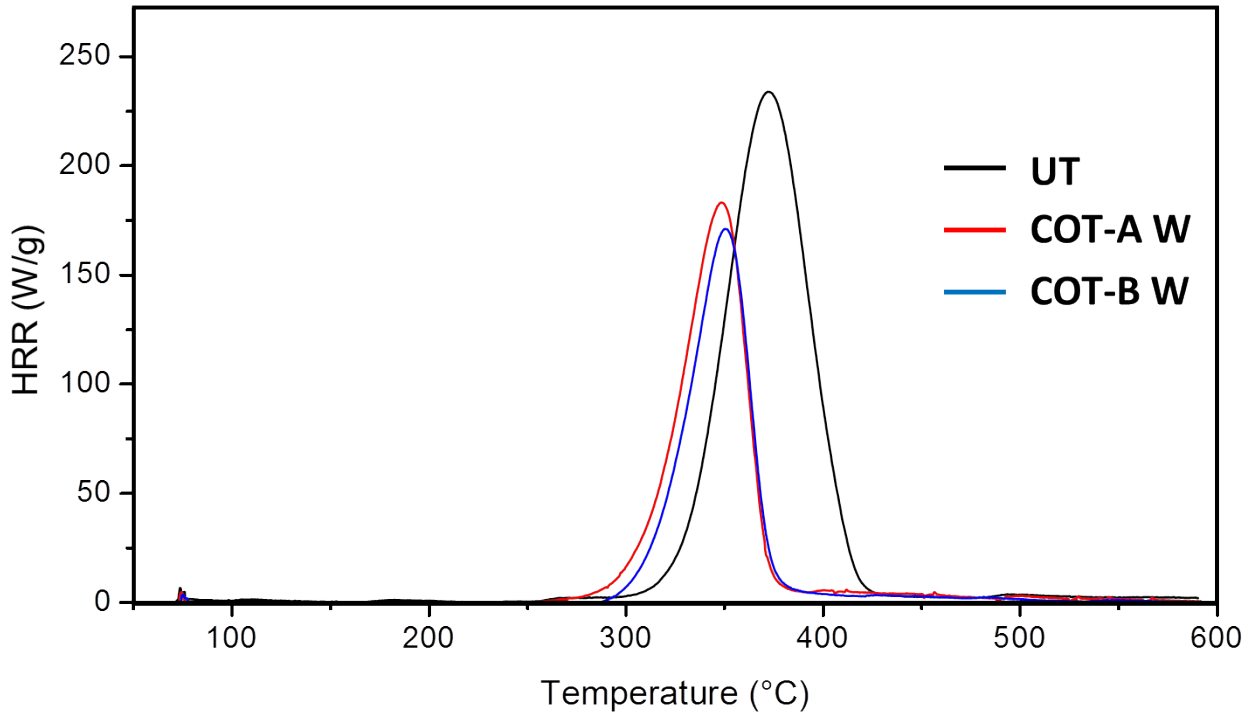


Table 1. Elemental analysis of treated fabrics.

Samples	C (%)	O (%)	Si (%)	N (%)	P (%)
Untreated	93.9	2.1			
COT-A	69.5	18.8	1.5	4.8	1.9
COT-B	75.7	13.2	1.3	5.7	0.8

Table 2: Thermogravimetric data of untreated and FR treated cotton in air.

Sample	T _{onset 5%} [°C]	T _{max1} [°C]	T _{max2} [°C]	T _{max3} [°C]	Residue at T _{max2} [%]	Residue at 750°C [%]
UT	328	-	419	556	37.5	0.5
COT-A	255	293	387	619	58.7	9.3
COT-B	270	287	385	625	60.0	13.5

Table 3: MCC data of untreated and FR treated cotton.

Sample	T_{PHRR} T_{max1} [°C]	T_{PHRR} T_{max2} [°C]	pHRR Q_{max2} [W/g]	Specific Heat release h_c [kJ/g]	HRC η_c [J/g-K]	Char Yield Y_p [g/g]	THR [kJ/g]
UT	-	383.9	253.7	11.5	250.3	0.04	12.0
SolA	249.3	345.6	78.7	3.5	77.0	0.31	4.8
SolB	252.3	348.6	76.5	2.7	74.7	0.35	4.2

Table 4. LOI values of untreated and treated cotton fabrics.

Sample	Unwashed samples			Washed samples		
	Measured	Calculated		Measured	Calculated	
	Values	Values		Values	Values	
	LOI	$t_{100\text{ mm}}$ [s]	LOI	LOI	$t_{100\text{ mm}}$ [s]	LOI
UT	19	152	19	19	152	19
COT-A	29	97	26	20	147	19
COT-B	29	114	27	21	128	19

Table 5. MCC data of untreated and fire-retardant treated samples after one washing cycles (COT-A W and COT-B W).

	T_{PHRR} $T_{max2} [^{\circ}C]$	pHRR Q_{max2} [W/g]	Specific Heat release h_c [kJ/g]	HRC η_c [J/g- K]	Char Yield Y_p [g/g]	THR [kJ/g]
UT	383.9	253.7	11.5	250.3	0.04	12.0
COT-A W	352.3	187.4	7.4	183.4	0.18	9.11
COT-B W	352.7	189.2	6.4	186.0	0.22	8.17

Table 6. Thermogravimetric data of fire-retardant treated and washed samples in air.

Sample	$T_{\text{onset 5\%}}$	T_{max1}	T_{max2}	Residue at	Residue at
	[°C]	[°C]	[°C]	T_{max1} [%]	750 °C [%]
COT-A W	340	391	604	54.6	1.8
COT-B W	309	384	579	55.9	2.9

HIGHLIGHTS

- Cotton samples coated with MEA-DPTES sol-gel showed flame retardant properties.
- MEA was able to neutralize the acidic conditions of DPTES sol before treating.
- MEA acted like nitrogen source in the cotton fabric hybrid coatings.
- LOI value of 29 classified treated samples as self-extinguishing materials.
- Silica matrix contributed to fix P- and N- based molecules onto cotton fabrics.