Carbohydrate Polymers 96 (2013) 296–304

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Intrinsic intumescent-like flame retardant properties of DNA-treated cotton fabrics

Jenny Alongi[a,*], Riccardo Andrea Carletto[b], Alessandro Di Blasio[a], Fabio Cuttica[a], Federico Carosio[a], Francesca Bosco[b], Giulio Malucelli[a]

[a] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Viale Teresa Michel 5, 15121 Alessandria, Italy
[b] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

ARTICLE INFO

Article history:
Received 15 February 2013
Received in revised form 8 March 2013
Accepted 21 March 2013
Available online 28 March 2013

Keywords:
DNA
Cotton
Flammability
Combustion
Green flame suppressants

ABSTRACT

In the present work, the effect of different DNA add-ons (namely, 5, 10 and 19 wt.%) has been thoroughly investigated as far as the flammability and the resistance to an irradiating heat flux of 35 or 50 kW/m^2 are considered. The results have shown that 10 wt.% is the minimum amount that allows reaching the self-extinguishment of cotton when a methane flame is applied. Furthermore, only 19 wt.% is able to confer resistance to the fabric towards an irradiating heat flux of 35 kW/m^2: indeed, the specimens tested under the cone calorimetry do not burn. Measurements of temperature runs as a function of time have clearly indicated that cotton, instead of burning, pyrolyses: indeed, because of the protective role exerted by DNA molecules, the deposited coatings have turned out to absorb heat, form char and induce its formation on the fabric, and finally to release inert gases.

1. Introduction

Although cotton is one of the most important textiles employed in the market, some of its applications can be limited due to its high flammability. As a consequence, the most efficient flame retardant systems currently available for this fabric are phosphorus-containing species that release phosphorus acids upon heating, which act as Lewis acids and promote the char formation (Bourbigot, 2008; Horrocks, 1986, 2003; Weil & Levchik, 2008), favouring the dehydration of the cotton fabric cellulose, and inhibiting its depolymerisation. More specifically, the performances of Proban® (i.e. (hydroxylmethyl)phosphonium salts) or Pyrovatex® (N-methylol phosphonopropionamide derivatives) are the main targets to fulfil (Kandola, Horrocks, Price, & Coleman, 1996; Weil & Levchik, 2008). Indeed, these benchmarks, having acceptable costs and meeting the current health, safety, and environmental issues, are showing acceptable technical performances and satisfying the flammability regulatory legislation (Horrocks, 2011; Lewin, 1983). Within the continuous seeking for novel cost-effective and environmentally sustainable flame retardants, the uses of biomacromolecules like proteins and nucleic or ribonucleic acids may represent a worthy alternative to the traditional approaches. Very recently, we have demonstrated that whey proteins can be used for achieving a homogeneous coverage of cotton fabrics and enhancing their flame resistance: these coatings have significantly sensitised the cotton degradation, giving rise to the formation of very high final residues (Bosco et al., 2013).

Alternatively, proteins, which bear groups with potential flame retardant features, can be considered extremely interesting and advantageous: in particular, caseins and hydrophobins, which contain phosphorus and sulphur elements, respectively, have exhibited a great potentiality as flame retardant systems for cellulosic substrates. Indeed, both the phosphate groups of caseins as well the disulphide bonds of hydrophobins have driven the cellulose pyrolysis towards the formation of char. As a consequence, an increased total burning time as well as a decreased total burning rate have been observed. In addition, the presence of the protein coating has also modified the resistance of cotton to a heat flux of 35 kW/m^2, with a significant reduction of heat release rate peak (−27 and −45% for caseins and hydrophobins, respectively) (Alongi et al., under review).

In this scenario, the complex double helix of DNA represents a potential and intrinsic intumescent-like flame retardant system, as it contains the three typical components of an intumescent formulation, namely: the phosphate groups, able to produce phosphoric acid, the deoxyribose units acting as a carbon source and blowing agents (upon heating a (poly)saccharide dehydrates forming char and releasing water) and the nitrogen-containing bases (guanine, adenine, thymine, and cytosine) that may release ammonia. The first results have clearly shown that after two applications of

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[*] Corresponding author. Tel.: +39 0131229337; fax: +39 0131229399.
E-mail address: jenny.alongi@polito.it (J. Alongi).

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http://dx.doi.org/10.1016/j.carbpol.2013.03.066

a methane flame for 3 s (in horizontal configuration), the DNA-treated cotton fabrics do not burn at all (Alongi et al., in press). This study has also pointed out that the DNA phosphate groups are able to generate phosphoric acid that catalyses the dehydration of cellulose, favouring its auto-crosslinking to an aromatic char and inhibiting the production of volatile species. To the best of our knowledge, this was the first attempt to exploit deoxyribonucleic acid as flame retardant, and in particular for cotton. However, there are still some issues that should be clarified: first of all, it seems that the DNA flame retardancy mechanism can also involve the deoxyribose units that produce further aromatic char, thus protecting the cotton fibres, acting as a physical barrier and hence limiting the heat, fuel and oxygen transfer between flame and polymer. At the same time, the decomposition of purine and pyrimidine bases could give rise to the formation of azo-compounds able to further induce the char development and the production of non-combustible gases (namely, N_2, CO_2 and CO).

Pursuing this research, the present work aims to elucidate the following issues: (i) the effect of different DNA add-ons on the flammability of the cotton, (ii) the resistance of the treated cotton fabrics to an irradiating heat flux, and (iii) the correlation between the morphology of the coatings with the resulting flame retardant properties of the treated fabrics. To this aim, three different add-ons (5, 10 and 19 wt.%, respectively) have been deposited on cotton by impregnation/exhaustion; the thermal and thermo-oxidative stability of the so treated fabrics as well as their resistance to the application of a methane flame or to an irradiating heat flux (namely, 35 or 50 kW/m^2) have been assessed by thermogravimetry, horizontal flame, Limiting Oxygen Index (LOI) and cone calorimetry tests. Finally, the collected data and thus the final properties of the fabrics have been discussed on the basis of the coating morphologies as observed by Scanning Electron Microscopy.

2. Experimental

2.1. Materials

Cotton (COT, 200 g/m^2) was purchased from Fratelli Ballesio S.r.l. (Torino, Italy).

DNA powder from herring sperm was purchased from Sigma–Aldrich S.r.l. (Milano, Italy) and stored at 4 °C before its application to the fabrics.

2.2. Impregnation/exhaustion of cotton fabrics with DNA solution

The DNA solution (2.5 wt.%) was prepared by slowly dissolving the DNA powder in acidified distilled water (pH 5.5) under magnetic stirring (300 rpm) at 30 °C for 30 min. Then cotton fabrics were impregnated for 1 min in a climatic chamber (30 °C and 30% R.H.); the excess of the solution was then removed with a rotary drum and the impregnated fabrics were dried to constant weight in a climatic chamber.

The total dry solids add-on on cotton samples (A, wt.%) was determined by weighting each sample before (W_i) and after the impregnation with the suspension and the subsequent thermal treatment at 30 °C overnight. (W_f), using a Gibertini balance (accuracy: $\pm 10^{-4}$ g). The uptake of samples was calculated according to the following equation:

$$A = \frac{W_f - W_i}{W_i} 100$$

The untreated and treated samples were coded as COT and COT_DNA_X, where X is 5, 10 or 19% and stands for the measured weight percentage add-on.

2.3. Characterisation techniques

The surface morphology of the treated samples was studied using a LEO-1450VP Scanning Electron Microscope (beam voltages: 5 and 20 kV for fabrics and residues, respectively); an X-ray probe (INCA Energy Oxford, Cu Kα 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-metallised.

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 analyzer was used, placing the samples (about 10 mg) in open alumina pans, in inert or oxidative atmosphere (gas flux: 60 ml/min). In the followings, $T_{\text{onset}10\%}$ and $T_{\max}$ will be defined as the temperature corresponding to a weight loss of 10% and the maximum weight loss rate, respectively. In addition, some tests in isothermal conditions in air were carried out: more specifically, the samples were heated from 50 to 350 °C, with a heating rate of 10 °C/min, and then kept at 350 °C for 1 h.

Flammability tests in horizontal configuration were carried out by applying a methane flame (the height of which was 25 mm) for 3 s on the short unclamped side of the specimen (25 mm × 100 mm), which was clamped in its three quarters by using a U-shaped metallic frame. These tests were repeated 3 times for each formulation. Total burning time (s), char length (mm), total burning rate (calculated as the ratio between the char length and total burning rate, mm/s) after the flame application, as well as the final residue (%) were evaluated. Limiting Oxygen Index (LOI) tests were performed with a FIRE oxygen index apparatus according to ASTM D2863 standard.

The combustion behaviour of square fabric samples (50 mm × 50 mm × 0.5 mm) was investigated by cone calorimetry (Fire Testing Technology, FTT). The measurements were carried out under two irradiative heat fluxes (35 or 50 kW/m^2), in horizontal configuration, following the procedure described elsewhere (Tata, Alongi, Carosio, & Frache, 2011). Such parameters as Time To Ignition (TTI, s), flame out (FO, s) and peak of heat release rate (pkHRR, kW/m^2) were measured. The experiments were repeated four times for each material investigated to ensure reproducible and significant data; the experimental error was within 5%.

Measurements of temperature profile as a function of time upon heating were carried out by using the cone calorimeter and following the procedure described elsewhere (Alongi & Malucelli, 2013). In particular, fabric specimens with a defined size (50 mm × 50 mm × 0.5 mm) were placed on a ceramic pad holed in the centre and kept 25 mm far from the irradiating source. Two separated thermocouples (stainless steel sheathed K-type thermocouples with 0.5 mm outer diameter) connected with the heating source were used for monitoring the temperature profile as a function of time (heat flux: 35 kW/m^2). A little discrepancy between the two thermocouples was found in the case of pure cotton, although it is not relevant for this study; the same phenomenon was almost negligible for all the treated fabrics.

Prior to flammability and combustion tests, all the specimens were conditioned at 23 ± 1 °C for 48 h at 50% R.H. in a climatic chamber.

3. Results and discussion

3.1. Morphology

The morphology of the DNA-based coatings deposited on cotton fabrics has been observed by Scanning Electron Microscopy (SEM). Fig. 1 shows the comparison between pure cotton (Fig. 1A) and the fibres treated with increasing DNA add-ons (namely, 5, 10

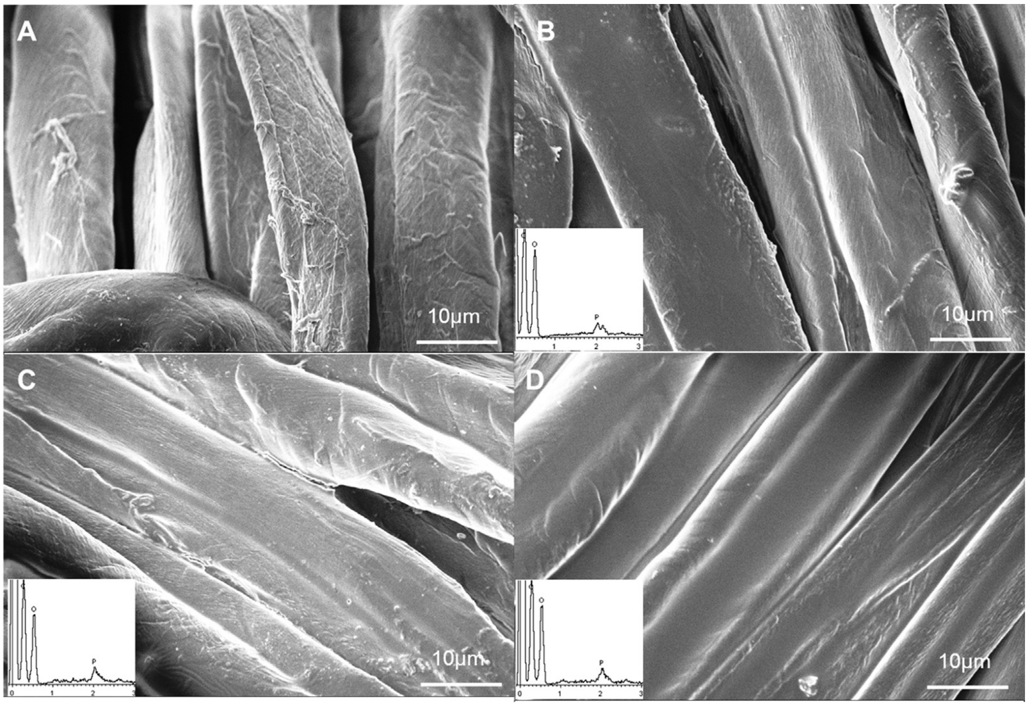

Fig. 1. SEM micrographs of COT_DNA_5% (A), COT_DNA_10% (B) and COT_DNA_19% (C) at 5000× and elemental analyses.

and 19 wt.% – Fig. 1B–D, respectively). From an overall consideration, the fibres appear completely and homogeneously covered by the coatings, regardless of the add-on, and thus of the DNA content. Comparing the different add-ons, it is worthy to mention that only in the case of 10 and 19 wt.% (Fig. 1C and D), the coating seems to form a continuous film on and in between the fibres, unlike COT_DNA_5%, where the coating does not fill up the interconnections between adjacent fibres (Fig. 1B). The elemental analyses reported in Fig. 1 inlets confirm the presence of C, O and P elements, main constituents of DNA macromolecule.

3.2. Thermal properties

The thermal and thermo-oxidative stability of the pure and treated cotton fabrics has been assessed by thermogravimetric analysis. Table 1 collects the data in nitrogen and air; Fig. 2 plots the TG and dTG curves of the samples under investigation.

As widely demonstrated (Alongi, Camino, & Malucelli, 2013; Price, Horrocks, Akalin, & Faroq, 1997) cotton pyrolyses in nitrogen through a single step process, during which the cellulose degradation follows two competitive routes, namely: depolymerisation of the main chain to produce volatile species (such as levoglucosan, furan and furan derivatives) and dehydration with further auto-crosslinking to form a thermally stable carbonaceous structure, known as *char*. As a consequence of these processes, upon heating cotton starts to degrade close to 335 °C ($T_{onset10\%}$, Table 1) losing 10 wt.%, and further evolves with a maximum weight loss rate at 366 °C (T_{max1}, Table 1) that corresponds to 54% weight loss. The presence of the coating is responsible of a strong sensitisation of the cellulose decomposition that is strictly dependent on the DNA add-on, as revealed by the $T_{onset10\%}$ values listed in Table 1 and well depicted in Fig. 2A. It is worthy to note that, by increasing the add-on (and thus the DNA content), $T_{onset10\%}$ and T_{max1} values decrease, while, at the same time, the residue found at T_{max1} is almost unchanged. This finding is ascribed to the phosphate groups of DNA that behave similarly to an inorganic phosphate salt like ammonium polyphosphate (APP), a common flame retardant system for cellulosic substrates. APP acts favouring the cellulose decomposition towards the char formation, thanks to the phosphoric acid released at about 260 °C. Analogously, DNA starts to decompose around 200 °C, releasing the same acid species, and to evolve towards a residue thermally stable up to 600 °C. By this way, the formation of the residue at T_{max1} is favoured, as well observable comparing the values listed in Table 1.

In air, the thermo-oxidation of cotton proceeds by an analogous route, with the only exception of the presence of a second degradation step at high temperatures (T_{max2}: 492 °C), ascribed to the oxidation of the char (formed during the first step) and of all the hydrocarbon species still present (Fig. 2B). Once again, the coatings are responsible of $T_{onset10\%}$ and T_{max1} anticipation as well as of the residue formation at T_{max1} that is thermally stable beyond 500 °C (T_{max2}, Table 1).

The effect of DNA as char former has been further investigated by combining TG measurements in dynamic and isothermal conditions, i.e. heating up the samples up to 350 °C (that can be considered as the minimum temperature, at which the char formation start to occur) and subsequently keeping them at this temperature for 1 h in air: Fig. 3 plots the weight loss as a function of time. In particular, in the above mentioned dynamic conditions, pure DNA starts to degrade at about 180 °C and further decomposes at 226 °C (see Table 1), releasing phosphoric acid and promoting the formation of a residue (66 wt.%, last column of Table 1), which is thermally stable at 350 °C for the overall duration of this test (i.e. in the subsequent isothermal conditions). These phenomena do not consider the water loss with the simultaneous denaturation of double strands occurring at 100 °C, as discussed by Yan and Iwasaki (2004). Thus, the same DNA can be considered as a char-former due to its intrinsic intumescent-like feature. Indeed, it is reasonable to suppose that DNA behaves similarly to an intumescent formulation, in which the phosphoric acid is released from either the cleavage of the phosphodiester bonds between two adjacent nucleosides or the cleavage of bonds between the phosphate group and C(5) of ribose ring. Meanwhile, the deoxyribose units may depolymerise or dehydrate (similarly to glucose rings of cellulose) giving rise

Table 1
Thermogravimetric data of pure cotton and DNA-treated cotton fabrics in nitrogen and air.

Sample	$T_{onset10\%}$ (°C)	T_{max1} [a] (°C)	T_{max2} [a] (°C)	T_{max3} [a] (°C)	Residue at T_{max1} [a] (%)	Residue at T_{max2} [a] (%)	Residue at T_{max3} [a] (%)	Residue at 600 °C (%)	Residue at 350 °C[b] (%)
Nitrogen									
COT	335	366	–	–	46.0	–	–	8.0	–
DNA	195	180	230	270	91.0	85.0	75.0	50.0	–
COT_DNA_5%	285	318	–	–	63.0	–	–	30.0	–
COT_DNA_10%	265	314	–	–	64.0	–	–	34.0	–
COT_DNA_19%	243	309	–	–	67.0	–	–	35.0	–
Air									
COT	324	347	492	–	45.0	4.0	–	0	13.0
DNA	171	180	226	333	90.0	85.0	69.0	49.0	66.0
COT_DNA_5%	282	313	506	–	65.0	19.0	–	8.0	30.0
COT_DNA_10%	263	302	511	–	69.0	24.0	–	13.0	35.0
COT_DNA_19%	238	299	515	–	68.0	29.0	–	19.0	42.0

[a] From derivative TG curves.
[b] From isothermal tests.

to an aromatic structure thanks to an auto-crosslinking process and releasing volatile species. At the same time, the decomposition of purine and pyrimidine bases can favour the formation of azo-compounds able to further induce the char development and the production of non-combustible gases (namely, N_2, CO_2 and CO) (Aubert et al., 2011; Pawelec, Aubert, Hoppe, Pfaendner, & Wilén, 2012; Wu & Chu, 2010).

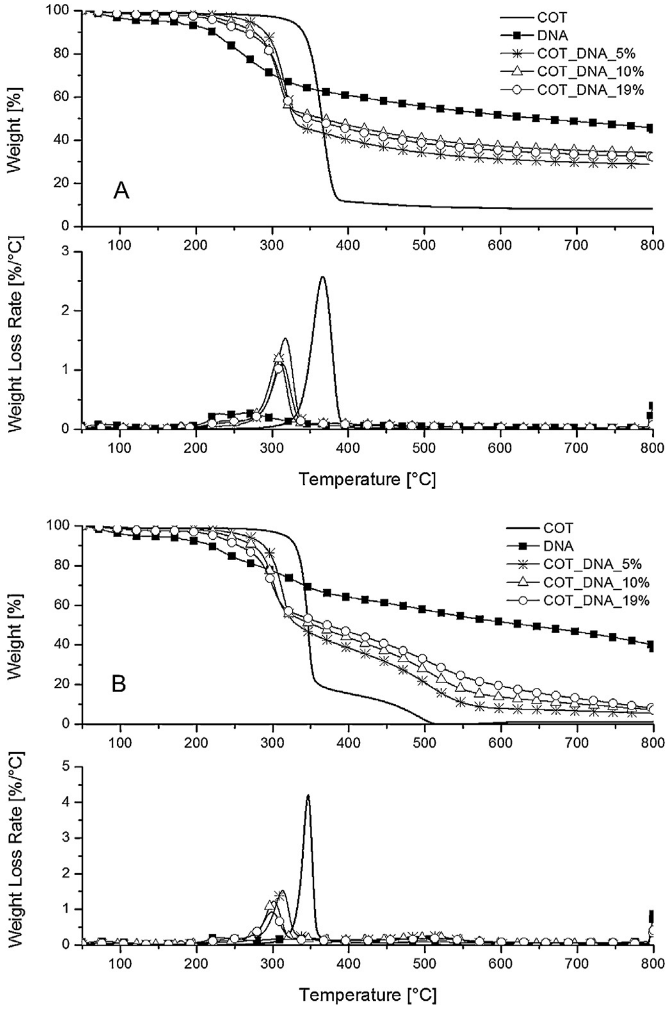

Fig. 2. TG and dTG curves of pure and treated cotton fabrics in nitrogen (A) and air (B).

When cotton is treated with a DNA-based coating, regardless of the add-on, a significant increase of the residue has been found at the end of the isothermal tests (namely, 30.0, 35.0 and 42.0% for COT_DNA_5%, COT_DNA_10% and COT_DNA_19%, respectively). Although it is not possible to discriminate the contribution of DNA and of cellulose on the char formation, a somehow chemical or physical interaction between the two species during their degradation in air can be guessed, since 42% residue for COT_DNA_19% is much higher as compared to the sum of the residues of pure cotton (13%) and of DNA (12%, calculated as the 19% of the DNA residue, Table 1).

3.3. Flame retardancy

In order to describe a realistic fire scenario, it is necessary 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 flux, developed as a consequence of the flame exposure. Therefore, the flame retardancy properties of pure and treated cotton fabrics have been measured through flammability tests in horizontal configuration, LOI measurements and combustion tests by cone calorimetry.

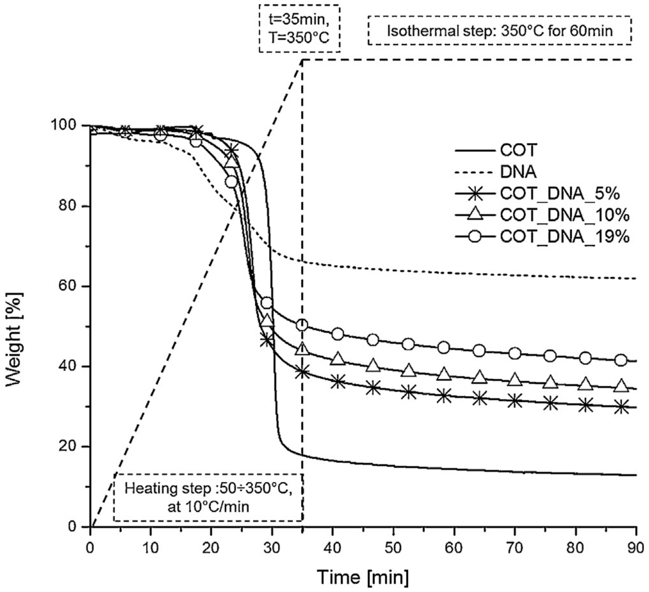

Fig. 3. TG curves of pure and treated cotton fabrics in isothermal conditions (350 °C) in air.

Table 2
Flammability data of pure cotton and DNA-treated cotton fabrics.

Sample	Total burning time (s)	Char length (mm)	Total burning rate (mm/s)	Residue (%)	Notes
COT	66	–	1.5	–	–
COT_DNA_5%	64	100	1.6	12.5	–
COT_DNA_10%	18	35	1.9	67.0	Flame out for all the three specimens
COT_DNA_19%	2	6	3.0	98.0	Flame out for all the three specimens

As already discussed (Alongi et al., in press), the application of a methane flame for 3 s to the untreated cotton causes a vigorous and rapid combustion of the specimen. At the end of the tests, no residue can be found (Table 2). On the contrary, COT_DNA_19% starts to burn very slowly and the self-extinguishment is reached within 2 s (Fig. 4). After this short combustion process, it is not possible to ignite the specimen again, following the standard procedure. The final residue and char length were of 98.0% and 6 mm, respectively. With a lower add-on (10 wt.%), the flame out is achieved again, but in this case the specimens ignite and burn for 18 s, leaving a residue of 67% and a char length of 35 mm. However, the flame is very small and it is difficult to assess whether the specimen burns because of the flame or for the occurrence of an incandescent zone. By further lowering the DNA add-on (5 wt.%), the fabric burns completely. Thus, we can conclude that 10 wt.% can be considered the minimum add-on (i.e. the minimum DNA content), necessary to reach the flame out of cotton, although the best performances are observed for COT_DNA_19%. The char zone of the residue left by the latter formulation has been observed by SEM and reported in Fig. 4. From an overall observation, the original texture of the fabrics is still maintained and the fibres appear almost intact. Furthermore, their surface turns out to be covered by small spherical structures finely dispersed, mainly consisting of C, O and P as assessed by EDS analysis.

These results have been further confirmed by LOI tests. Indeed, the LOI values of the treated fabrics increase from 18 (untreated cotton) to 23 (COT_DNA_5%), 25 (COT_DNA_10%) and 28% (COT_DNA_19%). These findings clearly indicate that the DNA coating can be considered an efficient flame retardant system.

In order to further assess this feature, cone calorimetry tests have been carried out. As far as the resistance to an irradiating flux is concerned, the first measurements were performed under two heat fluxes, namely 35 and 50 kW/m^2. Table 3 summarises the collected data.

As stated by Schartel and Hull (2007), after ignition, the cone calorimeter represents a well-defined flaming condition, forced by external radiation, typical for a developing fire scenario. The radiant heat flux can be varied between 0 and 100 kW/m^2, although 35 or 50 kW/m^2 are the most widely used, since they can be related to heat fluxes found in developing fires.

Under 50 kW/m^2 heat flux, cotton rapidly ignites and completely burns in 24 s (Table 3); the treatment with 19 wt.% of DNA strongly decreases the combustion time (9 s), as well as the pkHRR (−60%), leaving, at the same time, a significant residue (17%). As a matter of fact, 50 kW/m^2 heat flux appears too high for thoroughly studying the effect of the coating, since the corresponding combustion time is too short, as already discussed in the literature (Schartel & Hull, 2007). Therefore, the further measurements have been carried out under a lower heat flux (see Table 3).

Under a 35 kW/m^2 heat flux, cotton burns vigorously and quite rapidly in 30 s, while COT_DNA_19% does not ignite at all; indeed, this sample undergoes thermal-oxidation, leaving a 24% final residue that is still coherent and consistent. SEM observations show the original fabric texture (with intact fibres) and the presence of some spherical structures randomly dispersed within the burnt zone (Fig. 5). Probably, the action mechanism of the DNA coatings involves the formation of bubbles that blow up upon heat irradiation, releasing inert gases that dilute the volatile species and

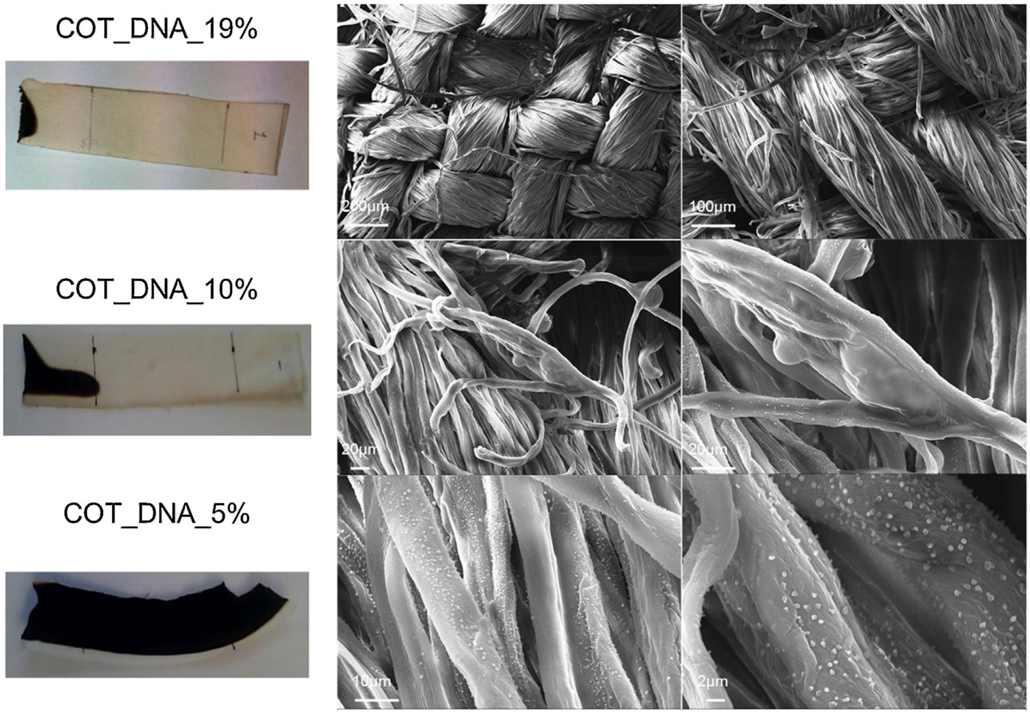

Fig. 4. Residues of the treated cotton fabrics after flammability tests and SEM micrographs of COT_DNA_19% residue after flammability tests.

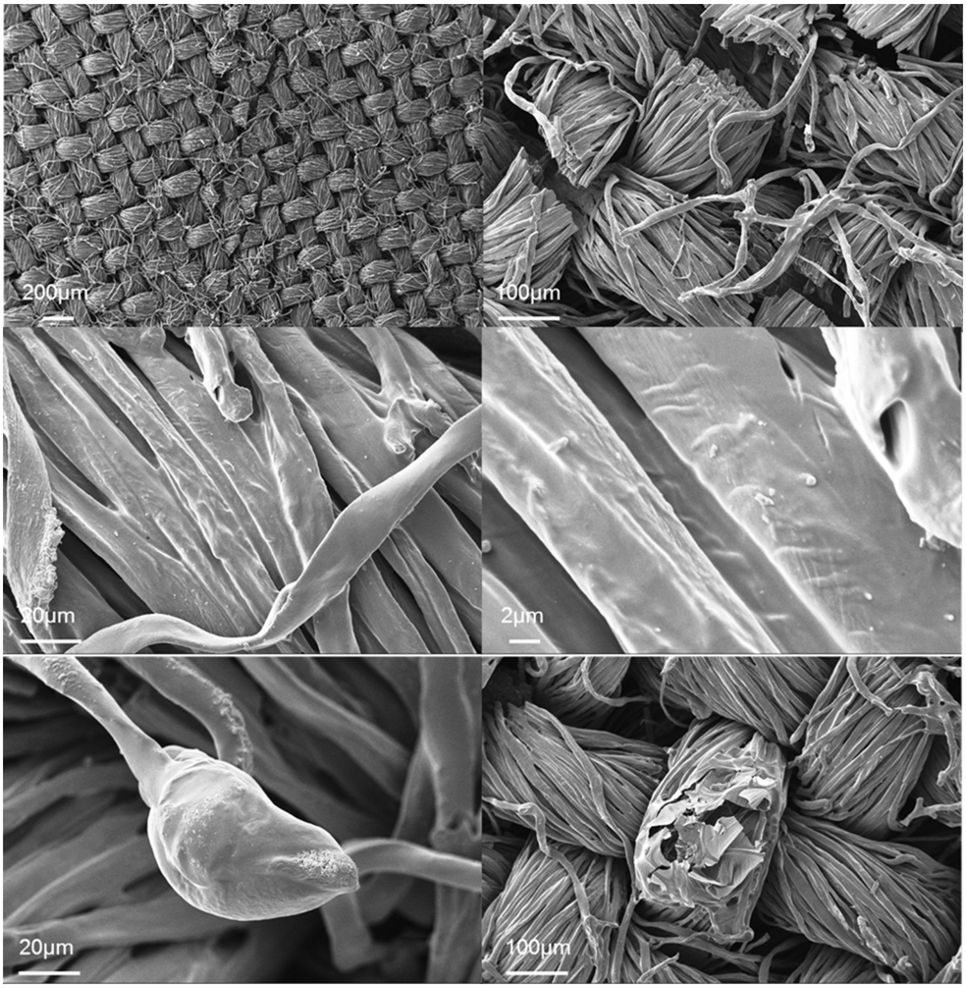

Fig. 5. SEM micrographs of COT_DNA_19% residue after the combustion tests under a heat flux of 35 kW/m^2.

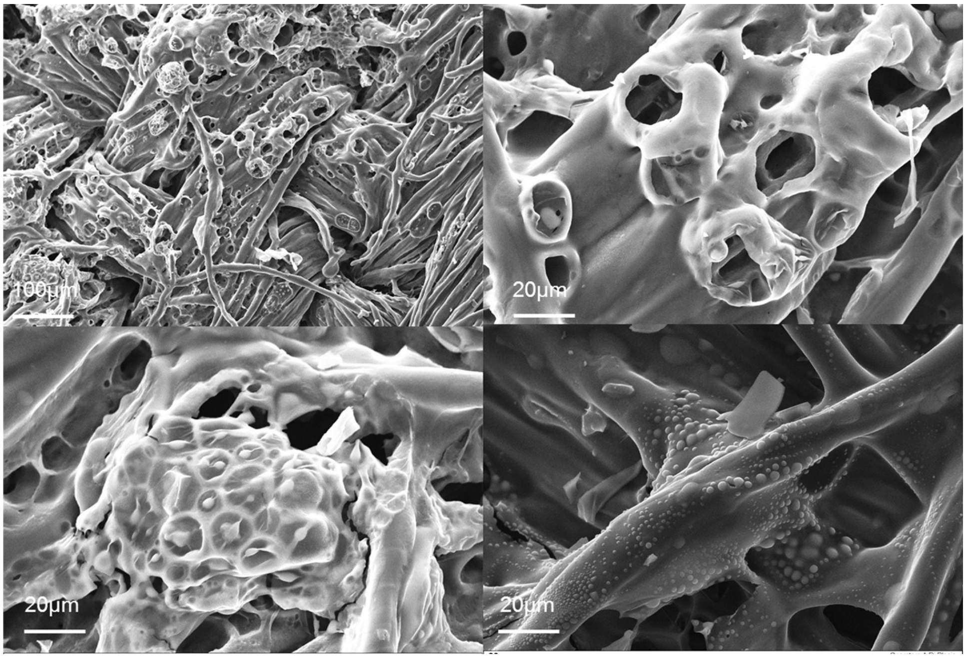

Fig. 6. SEM micrographs of COT_DNA_19% residue after the combustion tests under a heat flux of 50 kW/m^2.

Table 3
Combustion data of pure cotton and DNA-treated cotton fabrics.

Sample	TTI (s)	FO (s)	Combustion time (s)	pkHRR (KW/m^2)	ΔpkHRR (%)	Residue (%)
Heat flux = 50 kW/m^2						
COT	16	40	24	128	–	<3
COT_DNA_19%	10	19	9	51	−60	17
Heat flux = 35 kW/m^2						
COT	45	75	30	125	–	<3
COT_DNA_19%			No ignition			24
COT_DNA_10%	19	29	10	62	−50	15[a]
COT_DNA_5%	24	39	15	68	−56	15

[a] 2 specimens on 5 do not ignite.

Table 4
Collected data of pure cotton and DNA-treated cotton fabrics by thermocouple measurements.

Sample	Thermocouple 1				Thermocouple 2			
	TTI (s)	T_{TTI} (°C)	t_{max} (s)	T_{max} (°C)	TTI (s)	T_{TTI} (°C)	t_{max} (s)	T_{max} (°C)
COT	25	364	27	537	27	297	33	594
			37	580			41	637
			48	582			53	622
			66	490			63	539
COT_DNA_19%	No ignition		100	515	No ignition		110	520
COT_DNA_10%	No ignition		115	550	No ignition		115	490
COT_DNA_5%	20	332	27	680	20	302	28	690

prevent to reach the flammability limit. By this way, the treated cotton undergoes pyrolysis, instead of combustion. Fig. 5 shows a still intact bubble found in the residue. When the heat flux is high (namely, 50 kW/m^2), the heating rate is too rapid and so the coatings cannot act likewise: indeed, although the bubbles are formed, they do not blow up as rapidly as occurs when the heat flux is 35 kW/m^2 (Fig. 6).

Under 35 kW/m^2 heat flux, COT_DNA_5% and COT_DNA_10% are not able to block the ignition of cotton (Table 3); however, their combustion is very short and slow, as well visible comparing the combustion time of pure cotton with that of these treated fabrics (15 and 10 s vs. 30 s for COT_DNA_5%, COT_DNA_10%, and COT, respectively) and according to the reduction of the pkHRR value (around −50% for both samples). Once again, as already observed during the flame tests, the combustion proceeds because of the propagation of a small flame on the specimen.

The bubbles formed in COT_DNA_19% are also present in COT_DNA_10% and COT_DNA_5% residues after combustion, although their concentration is very low: this finding can be probably ascribed to the lower efficiency of such coatings in protecting cotton from the combustion as a consequence of the lower add-ons with respect to COT_DNA_19%.

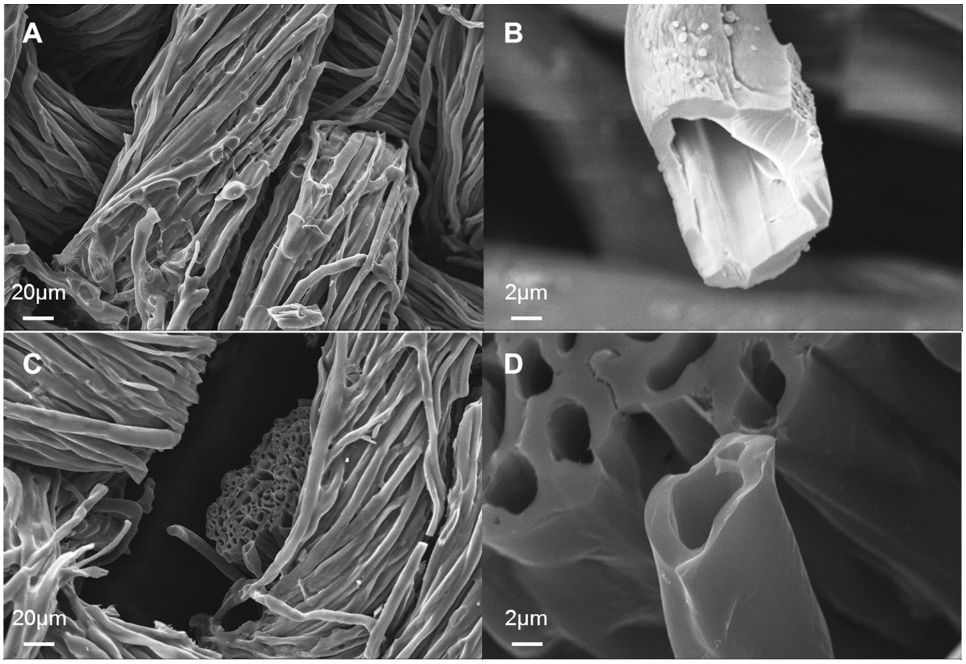

Fig. 7. SEM micrographs of COT_DNA_19% residues after the combustion tests under a heat flux of 35 (A and B) and 50 kW/m^2 (C and D).

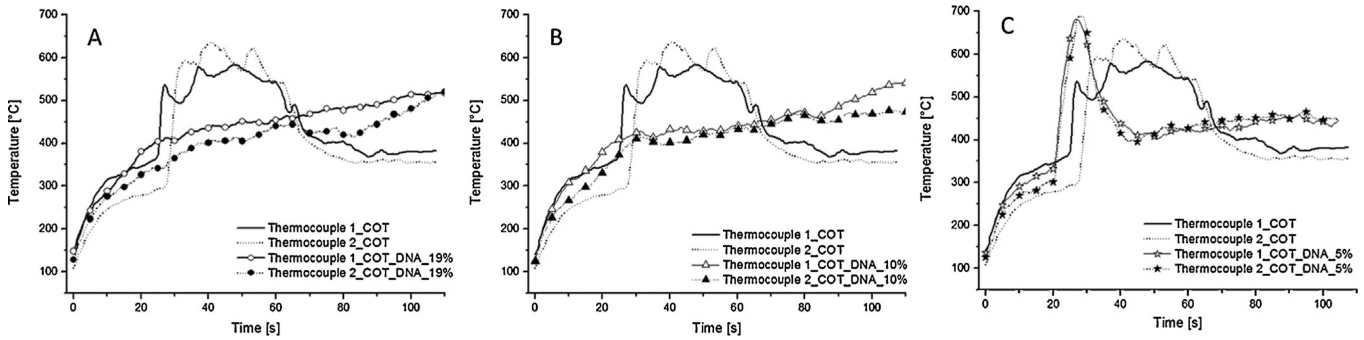

Fig. 8. Temperature profiles of COT_DNA_19% (A), COT_DNA_10% (B) and COT_DNA_5% (C).

Furthermore, Fig. 7 shows that, at the end of the tests, regardless of both heat fluxes and add-ons employed, the residue consists of hollow fibres. As examples, some micrographs of COT_DNA_19% residues after the combustion tests under a heat flux of 35 (Fig. 7A and B) and 50 kW/m^2 (Fig. 7C and D) are depicted. It can be concluded that 19 wt.% add-on is able to block the ignition of cotton under an irradiative flux of 35 kW/m^2, while lower add-ons are responsible for a drastic decrease of the combustion time and rate.

As discussed above, DNA has an intrinsic intumescent-like behaviour that induces the same macromolecules to form char. This process occurs only if DNA can absorb heat from the surrounding zone, and so it should be responsible of a drastic temperature decrease during the combustion. By this route, cotton is not enough irradiated from heat and thus does not ignite.

In order to confirm this hypothesis, some measurements aimed to monitoring the temperature profile as a function of time, under an irradiating heat flux of 35 kW/m^2, have been carried out (Table 4). The experimental set up and the temperature profiles of cotton, COT_DNA_19%, COT_DNA_10% and COT_DNA_5% are plotted in Fig. 8. More specifically, upon irradiation, cotton temperature slowly increases up to the ignition of the sample, subsequently it rapidly increases reaching roughly 550–600 °C (Fig. 8A). When cotton is treated with DNA (19 wt.% add-on), the starting temperature is slightly higher with respect to the pure fabric: however, the sample does not ignite and the temperature is almost unchanged (between 450 and 500 °C) for nearly 110 s, during which the sample pyrolyses, releasing white vapours. The same trend has been found for COT_DNA_10% (Fig. 8B). Probably, as already assessed for the flammability results, this add-on is close to the minimum limit that is necessary for suppressing the combustion, and therefore the sample does not burn during these measurements. On the contrary, when the DNA add-on is only 5 wt.%, the sample ignites earlier with respect to pure cotton, and reaches the maximum temperature of 700 °C; subsequently, the temperature decreases, notwithstanding its lower values as compared to pure cotton (Fig. 8C), also because the combustion proceeds only through the propagation of a small flame.

All the collected data have shown that the add-on (and thus the DNA content) plays a key role for reaching the flame out of cotton, regardless of the morphologies observed by SEM. Indeed, 19 and 10 wt.% add-ons have shown that all the fibres as well as their interconnections are completely and homogeneously covered by the coating; this does not occur when the add-on is just 5 wt.%.

Despite of the very promising flame retardant and suppressant features exhibited by the DNA coatings under study, these systems are currently showing a drawback, concerning their resistance and durability to washing treatments: indeed, the DNA coatings have come off when subjected to the ISO6330 standard. Therefore, this issue has to be carefully considered for the design of DNA-based flame retardants and will need further investigations.

4. Conclusions

In the present work, the effect of the presence of deoxyribonucleic acid (from herring sperm) on the flame retardancy of cotton has been thoroughly investigated. In particular, cotton resistance to a flame application for 3 s and to an irradiating heat flux has been assessed after the fabrics have been treated with 5, 10 and 19 wt.% of DNA.

The collected results have clearly shown that 10 wt.% represents the minimum add-on necessary to reach the flame out of cotton, when a methane flame is applied and that only 19 wt.% is able to confer resistance to an irradiating heat flux of 35 kW/m^2. Indeed, all COT_DNA_19% specimens tested in these conditions do not burn under the cone calorimeter, as well as only 2 on 5 samples treated with a lower add-on (10 wt.%). Furthermore, the evaluation of the temperature profiles as a function of time under an irradiating heat flux of 35 kW/m^2 has clearly demonstrated that cotton does not burn, but pyrolyses because of the presence of DNA molecules that absorb heat and release inert gases, hence decreasing the temperature of the fabric.

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). Prof. Giovanni Camino is acknowledged for the fruitful discussions, as well.

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