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Thermal stability and flame resistance of cotton fabrics treated with whey proteins

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ABSTRACT

It is well described in the literature that whey proteins are able to form coatings, which exhibit high mechanical and oxygen barrier properties, notwithstanding a great water vapour adsorption. These peculiarities have been exploited for applying a novel protein-based finishing treatment to cotton and for assessing the protein effect on the thermal and thermo-oxidative stability and on the flame retardant properties of the cellulosic fabric. Indeed, the deposited whey protein coatings have turned out to significantly affect the thermal degradation of cotton in inert and oxidative atmosphere, and to somehow modify its combustion when a flame has been applied. Furthermore, the influence of the secondary and tertiary structure of these proteins on the morphology of the deposited coating, and thus on the thermal and flame retardant properties of the treated fabrics, has been evaluated by performing a denaturation thermal treatment before the protein application.

1. Introduction

In the last few decades, the use of whey protein isolate (WPI) has received a remarkable interest for the production of films for food packaging. Indeed, whey protein components (α-lactalbumin and β-lactoglobulin) have been widely studied for their potential use as agents able to form edible and biodegradable films based on a waste stream from the cheese industry (Kokoszka, Debeaufort, Lenart, & Voilley, 2010). Usually, WPI products are obtained by ion exchange, followed by ultrafiltration or microfiltration and a subsequent ultrafiltration. This interest has been motivated by their high mechanical properties (Fairley, Monahan, German, & Krotcha, 1996; Khwaldia, Pereze, Banon, Desobry, & Hardy, 2004) and excellent oxygen barrier properties (Sothornvit, Olsen, McHugh, & Krochta, 2003, 2007). The film-forming properties of WPI have been applied for obtaining transparent, flexible, colourless, and odourless films. Sometimes, the incorporation of a minimal content of plasticizer (like glycerol and polyethylenoxide) within the protein mixture is necessary in order to favour the film formation and to reduce the film brittleness (Gounga, Xu, & Wang, 2007, 2010). Indeed, these plasticizers are capable to weaken intermolecular forces between adjacent protein chains: as a consequence, films having increased film extensibility and flexibility as well as decreased elasticity, mechanical resistance and oxygen/moisture barrier properties are obtained (McHugh, Avena-Bustillos, & Krochta, 1993; McHugh, Aujard, & Krochta, 1994; Hong & Krochta, 2003; Mate & Krochta, 1996).

In this context, the possibility to have remarkable oxygen barrier properties could represent a key issue when protein films (without plasticizer) are applied as coatings onto a polymeric substrate for two main reasons. First, these films could prevent, delay, or partially inhibit the thermal degradation of a polymer in inert and oxidative atmospheres. In addition, the water adsorption feature could be exploited for inhibiting the flammability of a thin polymeric substrate such as a fabric, since the absorbed water could partially dissipate the heat during the combustion and dilute the produced volatile species (Alongi & Malucelli, in press).

As far as plastics and textiles are concerned, the possibility of using green flame retardant systems for replacing the traditional additives is one of the driving forces that continue to stimulate the industrial and academic research toward novel and innovative solutions. In particular, the availability of a formaldehyde-free flame retardant system based on natural macromolecules such as proteins could be extremely interesting for a possible industrial application. Therefore, in the present work, the effect of the presence of a whey protein isolate coating (consisting of both folded and unfolded/denatured chains) on the thermal and thermo-oxidative stability and on the flame retardant properties of cotton fabrics has been thoroughly investigated by using thermogravimetry and flammability tests (in horizontal configuration), respectively. To the best of the authors' knowledge, this is the first example of

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Table 1
Amino acid profile of whey protein isolate.

Amino acid	Concentration [%]
L-cysteine	3.2
L-arginine	2.4
L-tyrosine	3.4
L-proline	3.6
Glycine	1.5
L-glutamic acid	14.2
L-aspartic acid	10.1
L-serine	3.6
L-threonine	4.3
L-valine	4.5
L-methionine	1.9
L-isoleucine	5.1
L-leucine	11.5
L-lysine	9.0
L-histidine	1.6
L-triptophan	1.9
L-alanine	4.6
L-phenylalanine	3.1

potential application of whey proteins to cotton fabrics for flame retardancy.

2. Experimental part

2.1. Materials

Cotton (COT, 220 g/m^2) was purchased from Fratelli Ballesio S.r.l. (Torino, Italy).

WPI powder (93.5 wt.% protein) was purchased from Anderson Research (Cervaro (FR), Italy); its overall composition also includes lipids (ca. 0.5 wt.%), carbohydrates (ca. 1 wt.%), ash (ca. 2.2 wt.%), and moisture (ca. 2.8 wt.%). Furthermore, the amino acid content is equal to 89.5 wt.% and its profile is listed in Table 1, as indicated in the data sheet provided by the supplier.

2.2. Application of whey protein coatings to cotton fabrics

The suspension of folded proteins (10 wt.%) was prepared by slowly dissolving WPI in distilled water under magnetic stirring (300 rpm) at room temperature for 10 min. The suspension of unfolded/denatured proteins was obtained from the folded protein suspension: first, pH was corrected to 7.0 with NaOH (0.1 M), then the suspension was heated up to 90 °C in a thermostatic bath under magnetic stirring (300 rpm) for 2 min, and finally cooled down to room temperature. Cotton fabrics were impregnated with the (folded or unfolded) protein suspensions for 1 min in a climatic chamber (30 °C and 30%R.H.); the excess of the suspension was then removed with a rotary drum and the impregnated fabrics were dried to constant weight in climatic chamber.

The treated samples were coded as COT_WP and COT_DWP, which refer to cotton fabrics treated with folded (WP) and unfolded/denatured proteins (DWP), respectively.

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 solution and the subsequent thermal treatment (W_f), using a Gibertini balance ($\pm 10^{-4}$ g). The uptake of COT_WP (ca. 25%) and COT_DWP (ca. 20%) was calculated according to the following equation:

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

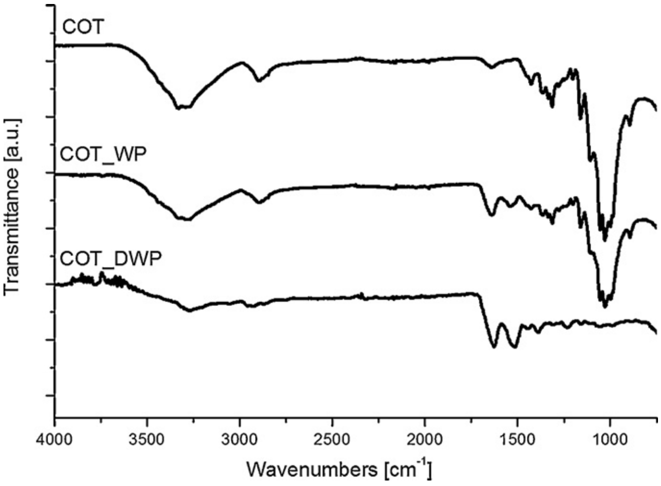

Fig. 1. ATR spectra of COT, COT_WP and COT_DWP.

2.3. Characterization techniques

The surface morphology of the treated samples was studied using a LEO-1450VP Scanning Electron Microscope (beam voltage: 5 kV); 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-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 analyzer was used, placing the samples (ca. 10 mg) in open alumina pans, in inert or oxidative atmosphere (gas flow: 60 ml/min).

Flammability tests in horizontal configuration were carried out by applying a methane flame for 5 s on the short side of the specimen (50 mm × 100 mm). These tests were repeated 3 times for each formulation. Total burning time and rate after the flame applications as well as the final residue were measured.

The chemical structure of the prepared samples and residues left after TG analyses was evaluated by Attenuated Total Reflectance (ATR) spectroscopy. ATR spectra were recorded at room temperature in the range 4000–600 cm^{-1} (32 scans and 4 cm^{-1} resolution), using a Frontier FT-IR/FIR spectrophotometer, equipped with a diamond crystal.

In order to determine the moisture content of the pure and treated cotton fabrics, a Karl-Fisher titrator (Mettler Toledo, model V20) was used: small pieces (ca. 0.1 g) were heated up to 150 °C and the moisture content was determined by using a mixture of methanol, potassium metabisulphite and I_2 as the titration system. The error was 0.5%.

3. Results and discussion

3.1. ATR spectroscopy

The effectiveness of the deposition of the whey protein isolate coatings on the cotton fabrics has been assessed through ATR spectroscopy. Fig. 1 shows the ATR spectra of COT, COT_WP and COT_DWP. First of all, the typical vibration modes of cellulose are well detectable in the pure cotton (namely, ν(OH) at ca. 3300, $\nu(CH_2)$ at 2900, δ(OH) at 1640, $\delta(CH_2)$ at 1425, δ(CH) at 1370, δ(OH) at 1310, ν(C—C) at 1020, and δ(OH) at 894 cm^{-1}). In the ATR spectra of COT_WP, two other peaks located at 1646 and 1533 cm^{-1} and substantially attributable to amide I and amide II vibrational

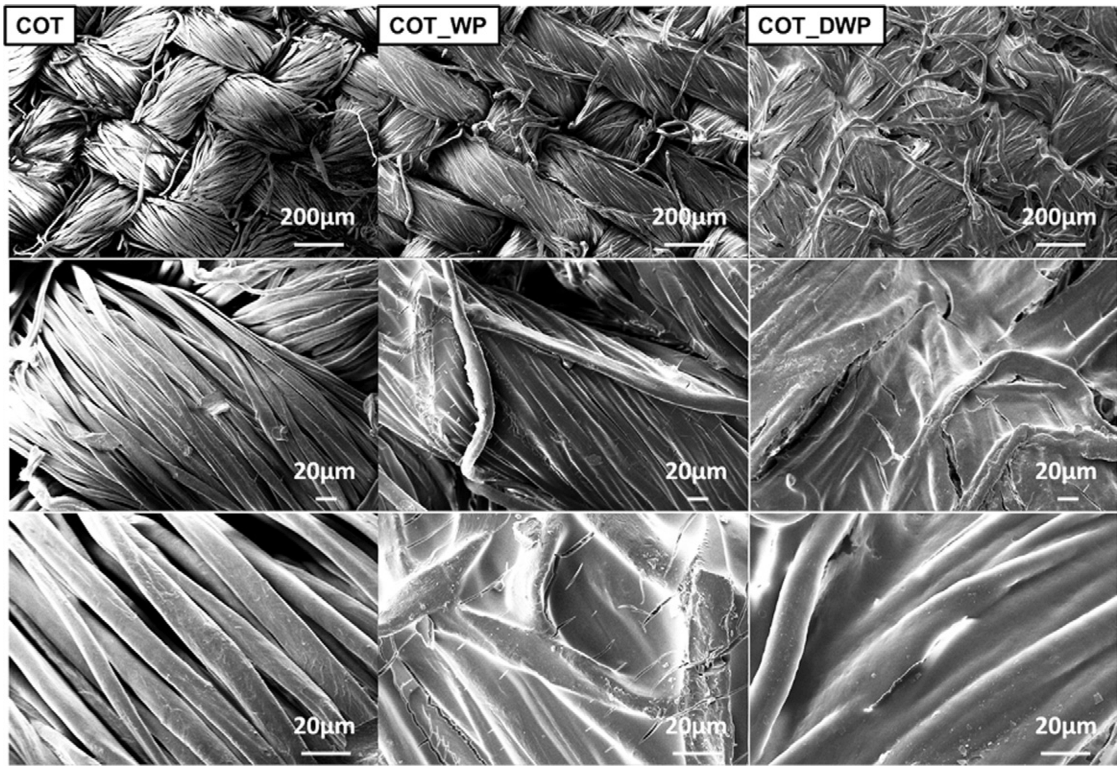

Fig. 2. SEM magnifications of COT, COT_WP and COT_DWP.

modes are observable because of the presence of the protein coating. The same peaks may also be ascribed to the presence of end amino acids – asymmetric and symmetric vibrations of the–NH_3^+ groups – (Socrates, 2004). However, the typical vibration modes of cellulose are still visible. On the contrary, when the proteins are denatured (COT_DWP sample), the unique bands still visible are those attributable to the vibrations of amide I and II groups (1621 and 1536 cm^{-1}, respectively). From a qualitative point of view, the deposited DWP-based coating turns out to be much thicker and regular than that of WP: this behaviour can be ascribed to the thermal denaturation, which is responsible of the disruption and possible destruction of both the secondary and tertiary structures of the proteins (i.e. the normal alpha-helix and beta sheets), and probably uncoils the protein itself into a random shape (Neurath, Greenstein, Putnam, & Erickson, 1944).

3.2. *Morphology of the cotton fabrics*

Scanning Electron Microscopy (SEM) coupled to elemental analysis (EDS) has assessed the morphology of the treated samples. Fig. 2 plots different magnifications of the pure and treated cotton fabrics. Both the protein types, folded and unfolded, are able to form a continuous and coherent film on the fibres, although some cracks are well visible when the proteins are still folded (COT_WP sample). Indeed, this finding has not been observed when the thermally denatured proteins (COT_DWP sample) are used: in this case, the film is probably more flexible and hence better adheres to the fibres, as the thermal denaturation causes a partial disruption of the tertiary and secondary structure of the proteins. Furthermore, the elemental analysis performed on COT_WP and COT_DWP samples has pointed out C, O, N and S elements as main constituents of the coatings. As an example, Fig. 3 shows the EDS mapping of these elements for COT_WP.

3.3. *Thermal and thermo-oxidative stability*

The thermal and thermo-oxidative stability of the treated samples has been assessed by thermogravimetric analysis and compared with that of pure cotton. Tables 2 and 3 collect the data in nitrogen and air, respectively; Figs. 4 and 5 plot the TG and dTG curves of the samples.

As already demonstrated (Alongi, Camino, & Malucelli, 2013; Price, Horrocks, Akalin, & Faroq, 1997), the thermal degradation of cotton in nitrogen proceeds by only one step, during which the maximum weight loss is found (Fig. 4). Indeed, cellulose pyrolyzes in nitrogen according to two alternative pathways, which involve (i) the decomposition of the glycosyl units to char at lower temperature and (ii) the depolymerization of such units to volatile species at higher temperature. The presence of the coating is responsible of a strong sensitisation of the cellulose decomposition, regardless of the protein type, as revealed by the $T_{\text{onset10\%}}$ values listed in Table 2 and well depicted in Fig. 4. Despite this finding, $T_{\max}$ is almost unchanged. The protein coating is responsible of the sensitisation of cotton degradation: indeed, the pure protein containing a high water amount start to decompose at ca. 100 °C giving rise to oligopeptides and amino acids that bear carboxylic groups able to catalyse the cellulose decomposition (Hanna, 1984).

As far as the thermo-oxidative stability is considered, cotton degradation usually occurs by three steps (Alongi et al., 2013). The

Table 2
Thermogravimetric data of untreated and treated cotton fabrics in nitrogen.

Sample	$T_{\text{onset10\%}}$ [°C]	$T_{\max}$ [°C][a]	Residue at $T_{\max}$ [%]	Residue at 750 °C [%]
COT	329	362	45.0	8.0
COT_WP	276	355	45.0	18.0
COT_DWP	294	366	45.5	17.0

[a] From derivative TG curves.

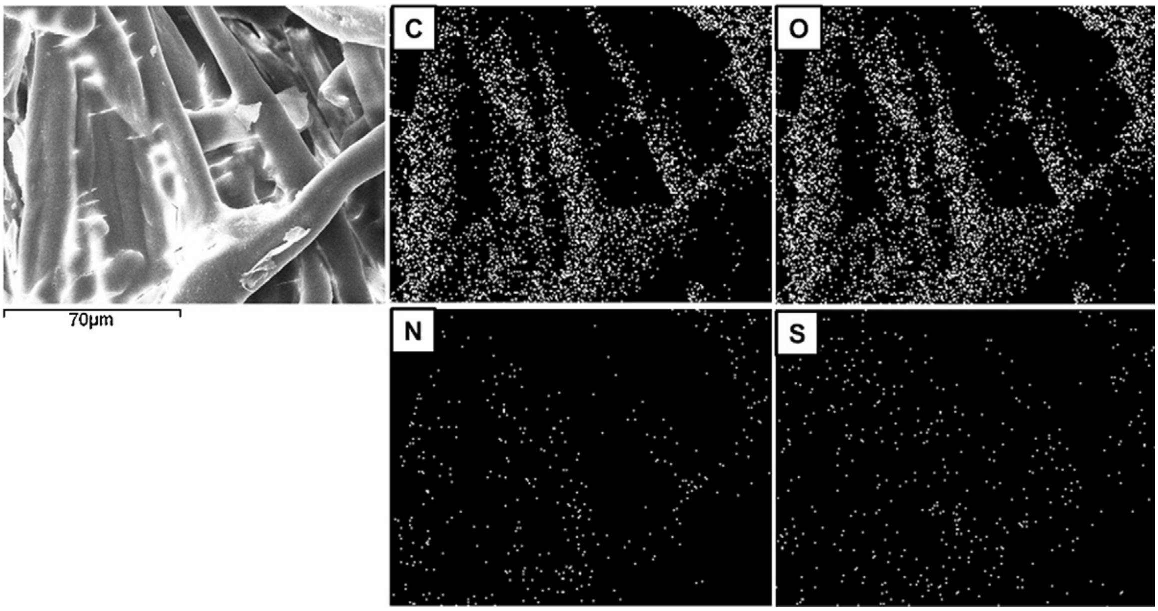

Fig. 3. EDS mapping of COT_WP.

first (at 300–400 °C) involves two competitive pathways, which yield aliphatic char and volatile products; during the second step (at 400–800 °C), some aliphatic char converts to an aromatic form, yielding carbon mono and dioxide as a consequence of the simultaneous carbonization and char oxidation. Within the last step (at ca. 800 °C), the char is further oxidized mainly to CO and CO_2. In the present work, two decomposition peaks are observable between 300 and 500 °C for cotton (namely, at 343 and 489 °C, Table 3 and Fig. 5). Once again, the presence of the coating sensitises the cellulose decomposition ($T_{onset10\%}$), but favours the formation of a thermally stable product after the first degradation step (*see* residue at T_{max1}, Table 3) that evolves at high temperatures by other two steps (T_{max2} and T_{max3}) and leaves a final residue slightly higher with respect to that of pure cotton. The third and last weight loss appears only for the treated fabrics (at 580 and 575 °C for COT_WP and COT_DWP, respectively), and therefore it can be attributable to the coating-substrate interactions. Indeed, at ca. 500 °C cotton leaves a negligible residue (*see* residue at T_{max2}) that evolves to mainly CO and CO_2. Analogously, WP and DWP films give a more thermally stable residue that completely degrades at ca. 490 and 510 °C, respectively (*see* inlet in Fig. 5). As a consequence, it is reasonable to hypothesize that the residue found for COT_WP and COT_DWP, stable up to ca. 580 and 575 °C (Table 3), could be ascribed to some chemical or physical interactions taking place among the species produced by the degradation of cellulose and proteins at high temperatures. It is unlikely that the residues formed at 550 °C are not aromatic and thus not thermally stable at high temperatures (*see* residue at 600 °C), as clearly indicated by the ATR spectra reported in Fig. 6: indeed, only vibrational modes of hydrocarbon species are detectable (namely, $\delta(CH_2)$ at 1457–1400 and 1459–1415, ν(C—C) at 1033 and 1035, and $\delta(CH_2)$ at 877 and 871 cm^{-1} for COT_WP and COT_DWP, respectively).

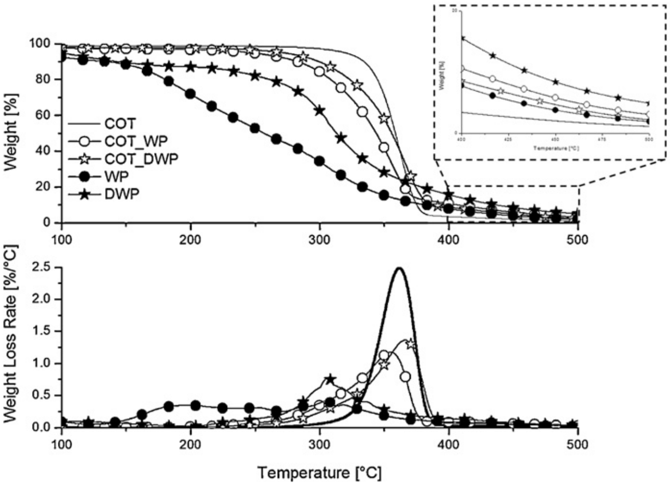

Fig. 4. TG and dTG curves of COT, COT_WP and COT_DWP in nitrogen.

3.4. Flame retardant properties

The flame retardant properties of the treated fabrics have been evaluated by horizontal flame tests: the collected data are listed in Table 4. Although both the coatings have been proven to increase

Table 3
Thermogravimetric data of untreated and treated cotton fabrics in air.

Sample	$T_{onset10\%}$ [°C]	T_{max1} [°C][a]	T_{max2} [°C][a]	T_{max3} [°C][a]	Residue at T_{max1} [%][a]	Residue at T_{max2} [%][a]	Residue at T_{max3} [%][a]	Residue at 600 °C [%]
COT	323	343	489	–	48.0	2.0	–	<1.0
COT_WP	283	341	487	580	57.0	14.0	2.5	1.5
COT_DWP	292	345	496	575	56.0	13.0	3.0	2.5

[a] From derivative TG curves.

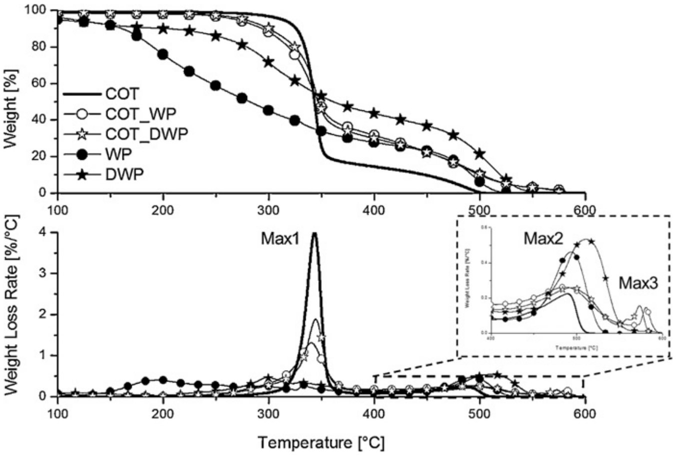

Fig. 5. TG and dTG curves of COT, COT_WP and COT_DWP in air.

Table 4
Flammability data of untreated and treated cotton fabrics.

Sample	Total burning time [s]	Burning rate [mm/s]	Residue [%]	Moisture content[a] [%]
COT	78	1.5	–	4.2
COT_WP	126	1.0	30	6.5
COT_DWP	133	1.1	5	6.0

[a] From derivative TG curves.

the total burning time and reduce the burning rate, only the WP-based coating is able to favour the formation of a significant residue (30 vs. 5% for COT_WP and COT_DWP, respectively). Indeed, by treating the fabrics with DWP, an extremely brittle and not completely coherent final residue is obtained. However, it is worth mentioning that the pure cotton quickly and vigorously burns without leaving any residue, while the treated fabrics, irrespective of the applied treatment (WP or DWP) burn more slowly in the presence of a small flame or afterglow. More specifically, the coatings seem to partially protect the cotton probably because they are able to hinder the oxygen diffusion and absorb the heat during the combustion. The moisture content may contribute to this mechanism, since the high water content found within the treated fabrics (4.2 vs. 6.5 and 6.0% for COT, COT_WP and COT_DWP, respectively) could partially inhibit the flame by absorbing the heat, although it is not capable to extinguish the flame. Indeed, the residues are further consumed by a bright incandescence.

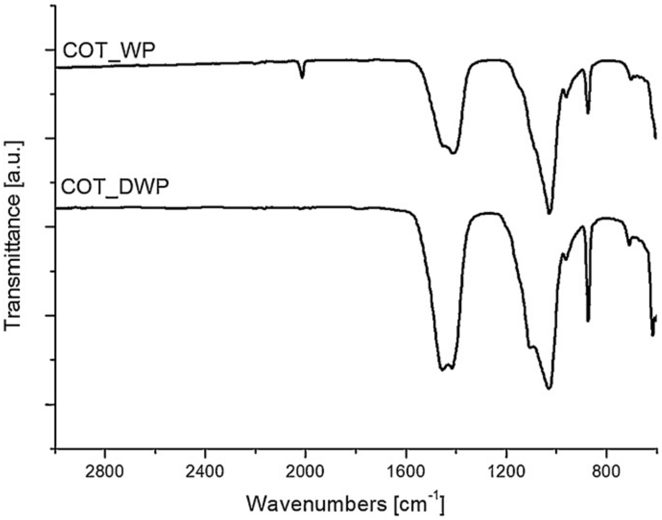

Fig. 6. ATR spectra of the residues (at 550 °C) left by COT_WP and COT_DWP.

At the end of the flammability test, the residues of COT_WP and COT_DWP have been examined by SEM: as well visible in Figs. 7 and 8, the protein-based films are able to somehow protect the cotton fibres, preserving the original texture of the fabrics.

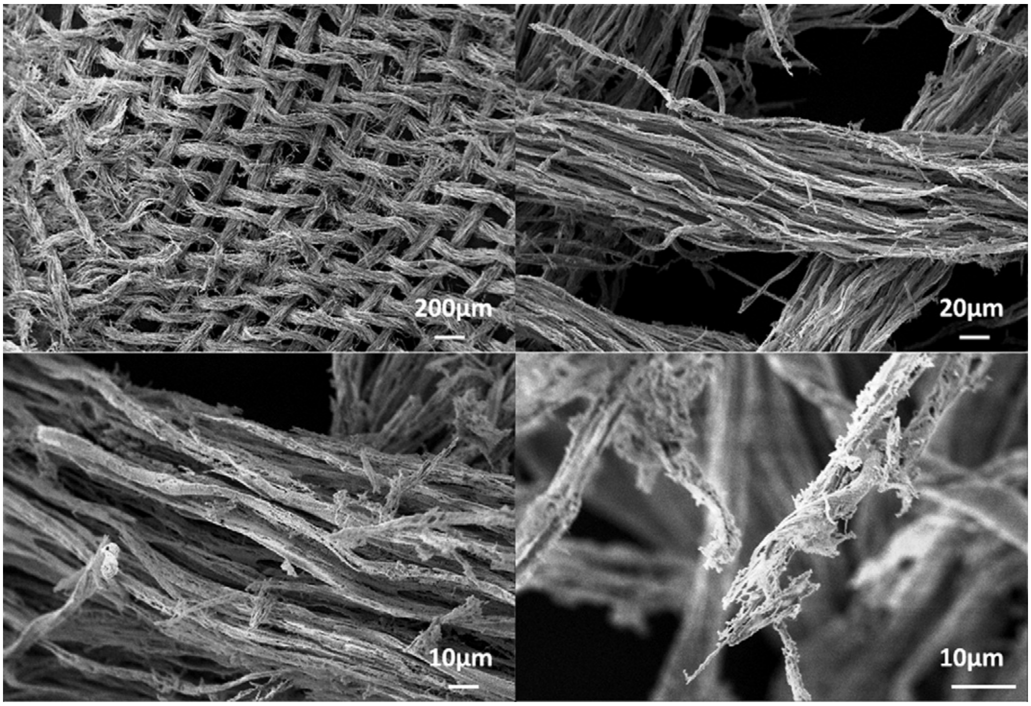

Fig. 7. SEM magnifications of the residues left by COT_WP after flammability test.

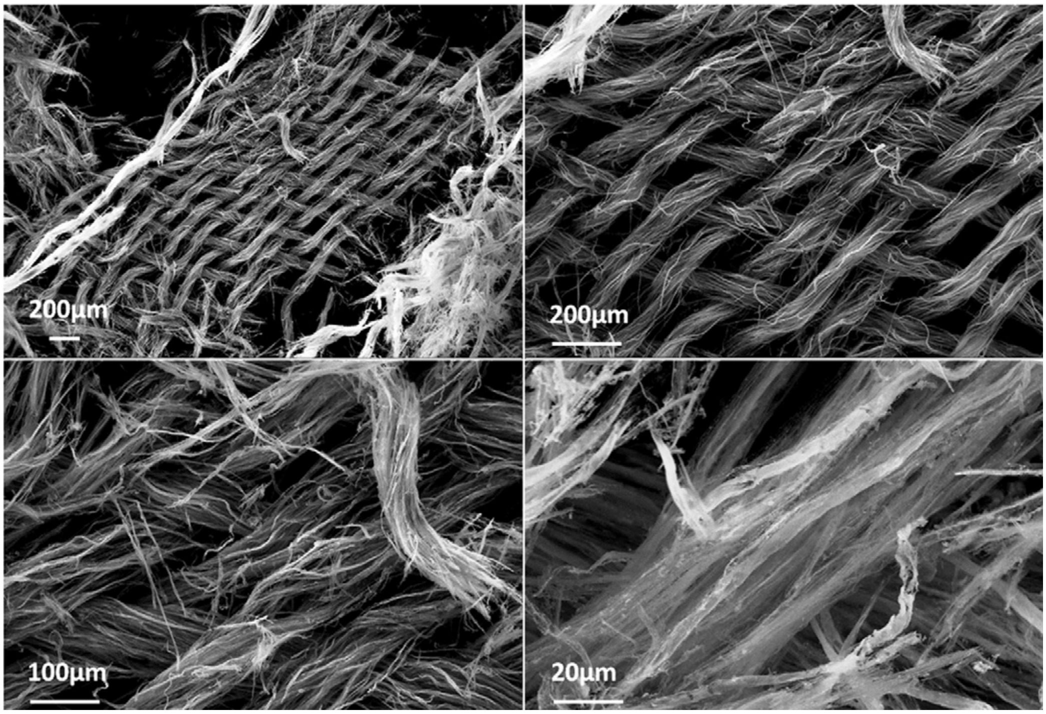

Fig. 8. SEM magnification of the residues left by COT_DWP after flammability test.

4. Conclusion

In the present work folded and unfolded whey protein isolate products have been successfully deposited on cotton fabrics, achieving a homogeneous coverage of these latter. The effect of the protein coating on the thermal and thermo-oxidative stability of the textile has been assessed by means of thermogravimetric analyses and horizontal flammability tests, respectively. More specifically, the presence of the protein coating, irrespective of its structure (folded or unfolded) has significantly sensitised the cotton degradation, but, at the same time, has assured very high final residues. Such features as good oxygen barrier properties and great water vapour adsorption have also been exploited for justifying the flame resistance of the treated fabrics, which have shown an increased total burning time, together with a reduced burning rate. Therefore, these systems may represent a novel and quite promising "green" finishing treatment for cellulosic substrates, also taking into account their origin from natural sources.

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