Thermal properties and decomposition products of modified cotton fibers by TGA, DSC, and Py–GC/MS

Polymer Degradation and Stability 228 (2024) 110937

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.journals.elsevier.com/polymer-degradation-and-stability

Thermal properties and decomposition products of modified cotton fibers by TGA, DSC, and Py–GC/MS

Mattia Isola [a,d], Giovanna Colucci [b,*], Aleandro Diana [a,d], Agusti Sin [c,d], Alberto Tonani [e], Valter Maurino [a,d]

[a] Chemistry Department, University of Torino, Via P. Giuria 5, Torino 10125, Italy
[b] Politecnico di Torino, Department of Applied Science and Technology (DISAT), Corso Duca degli Abruzzi 24, Torino 10129, Italy
[c] ITT Friction Technologies, Via Molini 19, Barge, CN 12032, Italy
[d] UNITO-ITT Joint Lab, via Quarello 15/a, Torino 10135, Italy
[e] Zanolo SpA, Via per Greggio, Arborio, VC 13031, Italy

ARTICLE INFO

Keywords:
Cotton fibers
Silanization
Fibers modification
Pyrolysis
Thermal stability

ABSTRACT

The thermal properties and pyrolysis decomposition paths of cotton fibers modified by different chemical treatments, a conventional functionalization with silane and a novel sulphation-phosphorylation approach, were studied. The effects on the fibers thermal behavior and decomposition products were investigated. The cotton fibers were characterized before and after the surface treatments by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and pyrolysis/gas chromatography–mass spectrometry (Py/GC–MS). Morphological investigation was also performed by SEM/EDS analysis to assess the treatment effects on the cotton fibers' surface. The silanization increases the cotton hydrophobicity and thermal stability, changing the pyrolysis mechanism, favoring depolymerization over dehydration and charring. On the contrary, sulphation-phosphorylation methods cause a decrease in the onset temperature and an increase of fire resistance, and charring yield. Thermal decomposition temperatures, weight losses, and pyrolysis mechanisms and products, were fully analyzed. The results can open the way on the use of modified cotton fibers in industrial fields where fireproofing is strongly desired.

1. Introduction

Cotton is considered the most common natural polymer, used in many applications fields due to its availability, flexibility, strength, chemical resistance, sustainability, and hydrophilicity [1–3]. It is the most important and widely grown crops in the world, mainly used for textile fibers purposes [1–3]. Moreover, the interest of using cotton fibers as reinforcing agents in composite materials, generally based on polymeric matrices, is constantly growing due to the several advantages associated with this natural polymer [4]. It is generally recognized that cotton fibers exhibit benefits such as availability, low price, together with desirable properties including biodegradability, softness, strength, and warmth [1–4]. However, their use in some industrial applications remains limited by the high structural variability, water sensitivity, poor compatibility with matrices, thermal stability, and high flammability [1–5]. The thermal stability, easy ignition, and rapid combustion of cotton fabrics represent a limitation in the production of fire-proof textiles based on cotton fibers [3,4]. Several approaches have been traditionally investigated for the chemical modification of cotton fibers together with the application of flame retardants to change their surface composition and improve the final properties. In some industrial fields such as building, automotive, and electronics, the behavior of cotton fibers under specific environmental conditions can play a crucial role [2]. The use of cotton in those sectors requires that their flame retardancy is improved. The pyrolysis and the thermal decomposition of cotton fibers should be accurately studied to understand their potential impact in a fire scenario.

Many studies are reported in literature on the modification of cotton fibers using silane coupling agents, e.g., tri-alkoxysilane structures bearing different organic functions. Different investigations were done to assess the impact of this chemical modification on the fibers surface thermal properties. This treatment involves the condensation of silanol groups with the hydroxy functions on the cotton fibers leading to the grafting of these chemical groups onto their surface [5–9]. Other

* Corresponding author.
E-mail address: giovanna.colucci@polito.it (G. Colucci).

https://doi.org/10.1016/j.polymdegradstab.2024.110937
Received 6 June 2024; Received in revised form 24 July 2024; Accepted 1 August 2024
Available online 2 August 2024

researchers focused their studies on completely different modification methods involving the sulphation or phosphorylation of cotton fibers to increase their thermal stability and fireproofing properties [10–16]. These procedures include the preparation of sulphonated and phosphorylated fibers for flame retardant materials, drug delivery matrices, and metal ion adsorbents for wastewater purification [11,12,15].

Sulphonated cotton fibers have been widely used to prepare negatively charged adsorbents for the removal of cationic dye pollutants for water treatment due to their high adsorption capacity [10,11].

A simple sulfuric acid treatment can be used to introduce sulfate half esters onto the surface of cotton or sulfation in aprotic solvents like N,N-dimethylformamide [10,11].

Phosphorylation of cotton can be achieved through both chemical modification and enzymatic phosphorylation [12–16]. Although both these methods can efficiently substitute hydroxyl groups onto the cotton surface, chemical methods are generally more cost-effective and faster. The phosphorylation reaction can be realized with different reagents, such as phosphoric acid, phosphorus pentoxide, ammonium phosphate, polyphosphate, and phosphoryl chloride in the presence of urea [12–16].

The present work aims to prepare different modified cotton fibers and to understand the structural and thermal decomposition changes induced by the chemical modifications. Cotton fibers were functionalized by means of conventional functionalization with 3-aminopropyltriethoxysilane (APTES) as coupling agent and by an innovative patented sulphation-phosphorylation approach. TGA, DSC, and Py–GC/MS were employed to investigate the unmodified and modified cotton fibers to obtain consistent and complementary information on the thermal decomposition. If several papers are available on the pyrolysis of raw cotton fibers focusing on the analysis of their combustion behavior, the literature on the combustion characteristics and relative combustion products of modified cotton fibers is limited. This manuscript analyses the changes in the pyrolysis and combustion processes of the modified cotton fibers. Morphological investigations were also carried out by SEM-EDS to study the effect of the functionalization methods on the cotton fibers surface and chemical composition. Moreover, the wettability of the modified fibers was estimated and compared with the unmodified ones, analyzing the relationship between these characteristics and the fiber chemical composition.

2. Materials and methods

2.1. Materials

Standard white cotton fibers, commercially available with a length of about 1 centimeter, were purchased by Goonvan Fibres Ltd (Devon, UK). 3- Aminopropyltriethoxysilane (APTES) was used as silane coupling agent and sodium dodecyl sulfate (SDS) was used as anionic surfactant for the modification reaction. Sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), ammonium hydroxide (NH_4OH), ethanol, hydrochloric acid (HCl), nitric acid (HNO_3), hydrofluoric acid (HF), and boric acid (H_3BO_3) were purchased by Merck All the reagents and solvents employed were at least of analytical purity and used as received without further purification.

2.2. Fibers treatments

Cotton fibers were modified according to three different modification methods, involving silanization, and sulfation-phosphorylation. The analyzed samples were named in the following as: Cotton, the as received cotton fibers, Cotton+APTES the fibers functionalized with APTES as silane coupling agent, Cotton COEX S and Cotton COEX P the fibers modified according to the different percentage of sulphation and phosphorylation employed during the modification process giving rise to the so-called COEX® cotton fibers.

2.2.1. Fibers modification by silane

Cotton fibers were soaked in NaOH solution at 50 °C for 4 h under magnetic stirring. The fibers solution was then neutralized with H_2SO_4 until pH=7. The fibers were then dried at room temperature overnight until a constant weight was reached. Subsequently, the cotton fibers were dispersed in a water solution containing SDS, as surfactant, at room temperature per 1 h under magnetic stirring. Then, 250 ml of ethanol, 3 ml of NH_4OH, and 5 ml of APTES were added to the solution. The solution was kept at room temperature under magnetic stirring for 24 h After the silane treatment, the fibers were washed several times with ethanol to remove the unreacted silane molecules, and finally dried even at room temperature until a constant weight was reached.

2.2.2. Fibers modification by sulphation-phosphorylation

The functionalization of cotton fibers by sulphation-phosphorylation treatment was carried out according to the experimental conditions reported in the European Patent Specification deposited [17], known as COEX® method. In brief, the cotton fibers were firstly immersed in a solution prepared by mixing at 50 °C water at 55% w/w, urea at 17% w/w, hydroxyethyl-imino-bis (methylene-phosphonic) acid at 20% w/w, and ammonium sulphamate at 8% w/w. Subsequently, they were centrifuged. Then, the yarn obtained after centrifugation was dried for 30 min at 80 °C and maintained at 115 °C for 2 h to obtain sulphation and phosphorylation of the cellulose. The resulting yarn was washed at 50 °C with detergent and water, dried again at 80 °C with forced air, and mechanically cut to obtain the final COEX® fibers.

COEX® is an innovative and completely natural fireproofing technology for obtaining fibers that, among the huge variety of flame-retardant chemicals available in the market, is totally biodegradable, not irritant, and not toxic.

3. Characterization techniques

3.1. Morphological investigations (OM, SEM, EDS)

The morphology of the untreated and treated cotton fibers was investigated using a Leica DMI 5000 M optical stereomicroscope and a Phenom™ XL Scanning Electron Microscope (Massachusetts, USA) at a voltage of 15 kV, after metallization with platinum using a Quorum Sputter Coater, Q150T S (Laughton, East Sussex), equipped with SEM-energy dispersive spectroscope (EDS).

3.2. Digestion procedure

To determine the presence of silicon and phosphorus on the different types of fibers it was performed an acid digestion by microwave (MLS-1200). Sample aliquots of 50 mg were digested with 5 ml of aqua regia and 2 ml of HF. It was applied the following program: 4 heating steps of 5 min each (250, 400, 600, 250 W, respectively) and a step 25 min of ventilation.

Then it was added 0.7 g H_3BO_3, and the samples were heated again for 5 min at 250 W followed by 25 min of ventilation. The resulting solutions were filtered with paper filters and diluted to 30 ml with HPW (High Purity Water). The solutions were analyzed with ICP-AES (Perkin Elmer Optima 2100 DV). The wavelengths of the analytes chosen were 251.611 for Si and 213.617 for P. Each sample was digested in three replicates.

3.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed by using a Mettler-Toledo TGA 851e instrument (Columbus, OH, USA) from 25 to 800 °C with a heating rate of 10 °C/min, in air and argon. The TG curves were normalized to the unit mass of the samples, and the DTG curves calculated on their thermograms.

3.4. Differential scanning calorimetry (DSC)

The thermal properties of the cotton fibers were evaluated by differential scanning calorimetry (DSC), using a DSC 214 Polyma Machine (Selb, Germany) from −50 to 450 °C, in nitrogen atmosphere (40 ml/min). The heating/cooling rate was maintained constant at 10 °C/min.

3.5. Pyrolysis-GC/MS

Pyrolysis experiments were performed using a micro-furnace pyrolyzer (EGA/PY-3030D, Frontier Laboratories Ltd., Japan) interfaced to a gas chromatograph-mass spectrometer (8890 and 7000D, Agilent Technologies, Inc., USA)

The gas chromatograph was equipped with a 30-meter, 0.25 mm ID fused silica capillary column coated with 0.25 μm film thicknesses of 5 % diphenyl 95 % dimethylpolysiloxane (Agilent HP5-MS). Helium was used as the carrier gas, (1 ml/min flow rate). For each type of cotton, the same sample quantity of 0.10∓0.005 mg was pyrolyzed. The samples were pyrolyzed at 600 °C for 0.20 min. Both the Py-GC interface and the injector temperatures were set at 300 °C. Injection was performed in split mode with a 1:100 ratio. The following oven temperature ramp was used: 40 °C for 2 min, ramp to 320 °C at 15 °C/min, and isotherm at 320 °C for 10 min. The total runtime was 30 min.

Temperatures of GC/MS transfer line, ion source, and quadrupole mass analyzer were set at 280 °C, 230 °C, and 150 °C, respectively. The mass spectrometer was operated in full scan mode (m/z range 29–600, 5 scans/s). The pyrolysis products were identified through spectral library search (NIST21) with a minimum match of 90 % for compound assignment.

3.6. Water contact angle measurement

The water contact angle of the unmodified and modified cotton fibers was measured using a contact angle analysis equipment OCA20 Data Physics. A drop of 10 μL of distilled water was syringed onto the fiber's surfaces, using an electronic syringe Hamilton DS500/GT, with a dosing rate of 5 μl/s. The image of the drop was immediately captured and analyzed to yield a contact angle value. The measurements were carried out on five different areas for each sample and the average value reported.

4. Results and discussion

4.1. Morphology of cotton fibers

Examination of the morphology of unmodified and modified cotton fibers was carried out by using an optical stereomicroscope, providing insights into the structural changes that occur due to modifications (Fig. 1). The images evidence the typical cotton fiber's morphology, characterized by tiny threads organized in lamellae randomly dispersed, extremely long in comparison with their widths. No relevant modifications in morphology for all the fibers samples are observed, independently from the modification occurring on their surface.

SEM analysis provides a more detailed and high-resolution view of their surface structures and modifications. Fig. 2 shows SEM micrographs of pure cotton fibers (a), fibers modified by silanization (b), and by sulphation-phosphorylation methods (c) and (d), collected at 500X of magnification. SEM images of silane treated cotton fibers (b) evidence a slightly smoother surface compared to that of untreated fibers (a). This difference can be caused by the chemical modification treatment, which can remove part of the hemicellulose fraction of the cotton structure. As clear, the presence of APTES does not affect the surface morphology of cotton fibers, but it influences the chemical composition of their surface [8,9].

SEM micrographs of Fig. 2 relative to the fibers modified by the different sulphation-phosphorylation conditions, (c) and (d), also evidence that even the other modification methods do not affect the fibers surface morphology. The fibers functionalized by sulphation-phosphorylation methods have the morphology of typical cotton fibers, where the width of the fibers slightly increases with respect to the unmodified fibers, as shown in Fig. 2 (c and d). However, COEX® fibers show a distinct coating on their surface stemming from the chemical modification which creates an abrasion resistant chemically active layer [17]. This can be put in evidence from the different intensity of the light

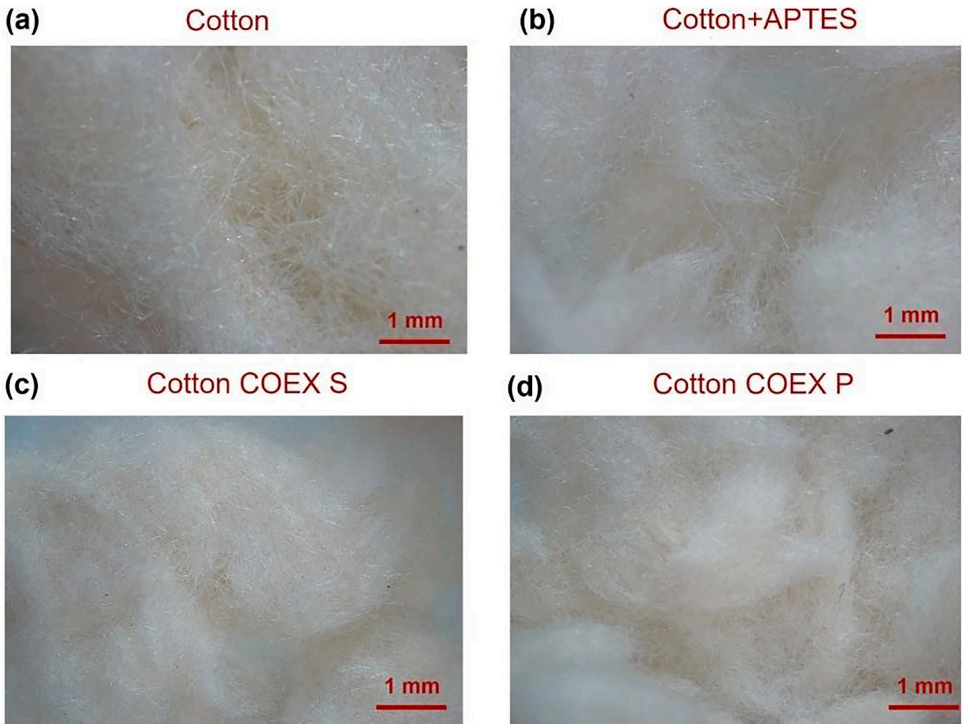

Fig. 1. Optical images of unmodified and modified cotton fibers.

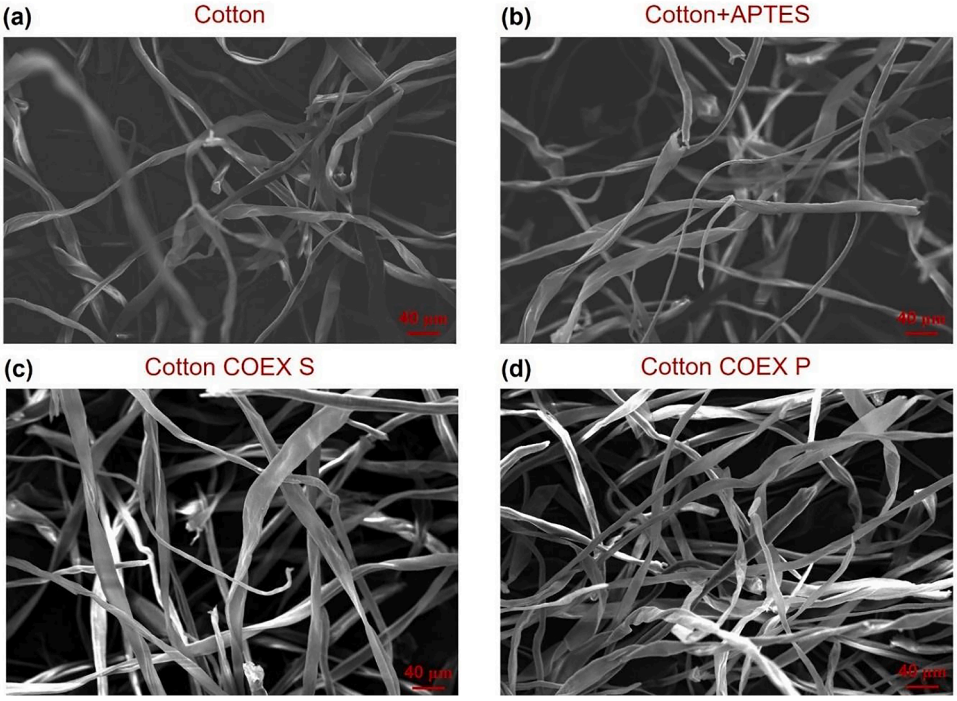

Fig. 2. SEM images at 500X of unmodified and modified cotton fibers.

the modified fibers show with respect to the unmodified ones.

SEM investigation was also carried out to verify the functionalization of cotton fibers through the EDS analysis onto their surface. The representative EDS spectra of unmodified and modified fibers are presented in Fig. 3. The EDS spectrum of cotton fibers shows the presence of strong peaks of carbon and oxygen as they are the major elements of cotton fibers, as visible in Fig. 3(a). An intense peak relative to silicon was detected for fibers modified with APTES, revealing a percentage of silicon atoms of about 19.44 %, on the surface of the fibers functionalized with silane, as clearly shown in Fig. 3(b). Fig. 3 (c and d) show the EDS analyses of the surfaces of the cotton fibers modified by sulphation-phosphorylation method performed in different conditions.

The presence of silane and phosphorus atoms grafted onto the cotton fibers surface was also confirmed by means of acid digestion tests [18], which led to the determination of their concentration, expressed in g/kg, as reported in Fig. 4.

The results obtained by acid digestion show a concentration of Si of 9.45 g/kg for the fibers silanized with APTES compared with the values of the untreated fibers, of around 1.05 g/kg.

Moreover, the acid digestion carried out on cotton fibers modified by sulphation-phosphorylation methods confirms the presence of phosphorous in different concentrations. P content in COEX S was 4.93 g/kg whereas in COEX P was 12.86 g/kg, around 2.5 times more. The data confirm the minimal increase in ash quantities measured with TGA for treated cottons.

4.2. *Thermal properties of cotton fibers*

The thermal stability of unmodified and modified cotton fibers was evaluated by thermogravimetric analysis. The thermal behaviors of the different samples determined in oxidant (air) and in inert (argon) atmosphere are reported in Fig. 5. As well-known from the literature, the thermal degradation of the unmodified cotton fibers involves four main steps, i.e., moisture evaporation, hemicellulose decomposition, cellulose decomposition, and lignin decomposition [19,22,23]. Looking at the thermogram of the unmodified cotton fibers and its relative first derivative curve performed in air, it is possible to see the presence of a small peak at lower temperature (48 °C) due to the desorption of the moisture absorbed on the fibers surface. The main degradation peaks are visible at 311 °C and 394 °C for the hemicellulose and cellulose fractions, and 431 °C for the lignin fraction, the most difficult part to decompose. Cotton fibers thermal behavior also shows 3 wt.% of residue content at 800 °C, which can be attributed to the presence of inorganic compounds present in the cotton fibers structure. The functionalized cotton fibers show completely different thermal behaviors, with respect to the unmodified fibers. Fig. 5 highlights the presence of a main degradation peak at 318 and 490 °C for the cotton fibers modified by silane, probably due to the decomposition of the amino silane grafted onto the cotton fibers surface. The complete disappearance of the degradation peak related to the cellulose was evident. This significant change can be attributed to the chemical modification process that influences the degradation of the cellulose component, leading to a reduction of the decomposition temperature [23,25].

A different trend can be also seen for the cotton fibers modified by sulphation-phosphorylation reaction. The thermal behavior of samples presents the typical peak at 48 °C due to the moisture evaporation, and a major degradation peak with a maximum at 237 and 247 °C the Cotton COEX S and Cotton COEX P, respectively, caused by the different cellulose decomposition induced to the different modification reaction conditions. The absence of the degradation peak related to the cellulose fraction of the cotton fibers was also evident.

Moreover, the white residue content of the modified fibers curves under oxidizing atmosphere is slightly higher than the value of the raw cotton fibers. In fact, the residue values for the fibers modified with silane and sulphation-phosphorylation reactions are 4 and 5 wt.%, respectively. The degradation temperatures at which there is the 5, 10, and 50 percent of weight loss (T_5, T_{10} and T_{50}), the maximum degradation peaks temperatures ($T_{max\ deg}$) and the ash content percentages are summarized and listed in Table 1.

TGA of cotton fibers, performed in an inert atmosphere using argon, and their first derivative curves, as reported in Fig. 5 (c, d). The fibers decomposition occurs in two separate steps.

All the fibers samples present the typical peak related to the moisture evaporation at around 60 °C, followed by a second decomposition peak

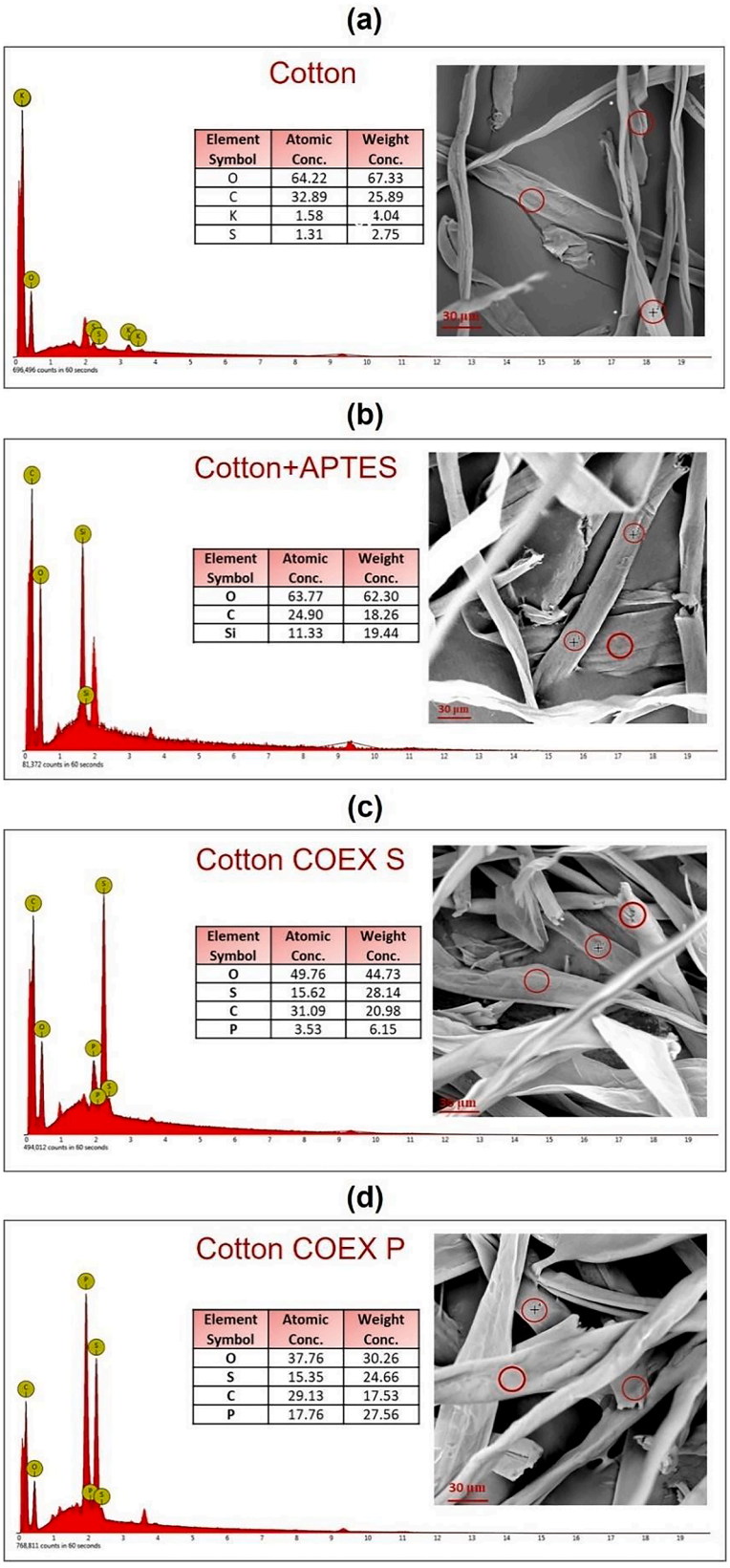

Fig. 3. SEM micrographs and EDS spectra of unmodified and functionalized cotton fibers.

starting at temperatures higher than 200 °C and finishing at around 400 °C with a maximum fixed at 338 °C for the unmodified fibers, due to the depolymerization of the cellulose of the cotton fibers. The most significant weight loss for the modified fibers, estimated by DTG curves, was found at 360, 237, and 247 °C for the treated fibers. The functionalization with silane led to a slight increase of the thermal stability, intended as the onset of the processes leading to gaseous product formation. Depolymerization and dehydration processes of cellulose start

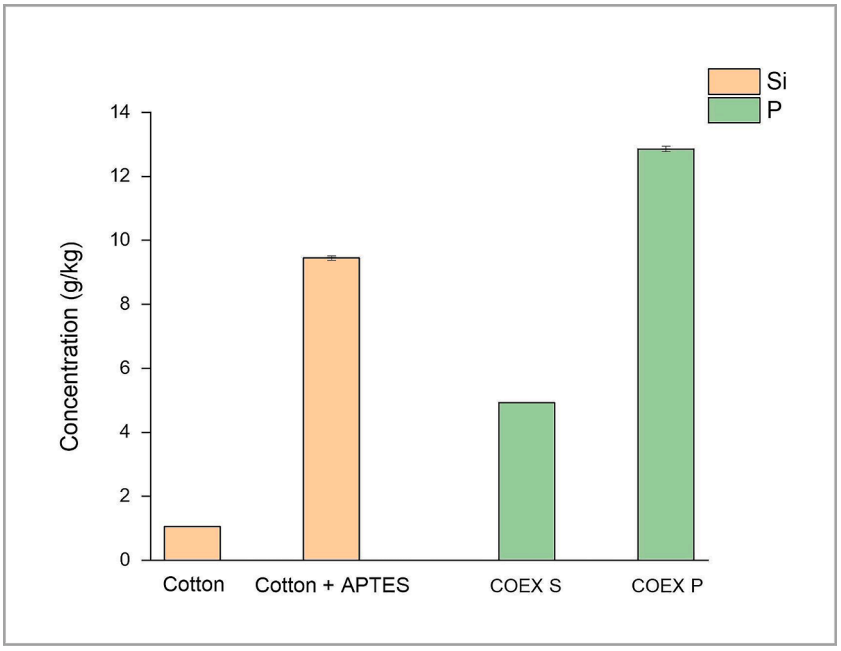

Fig. 4. Acid digestion results of unmodified and modified cotton fibers. Black bars indicate the standard deviation.

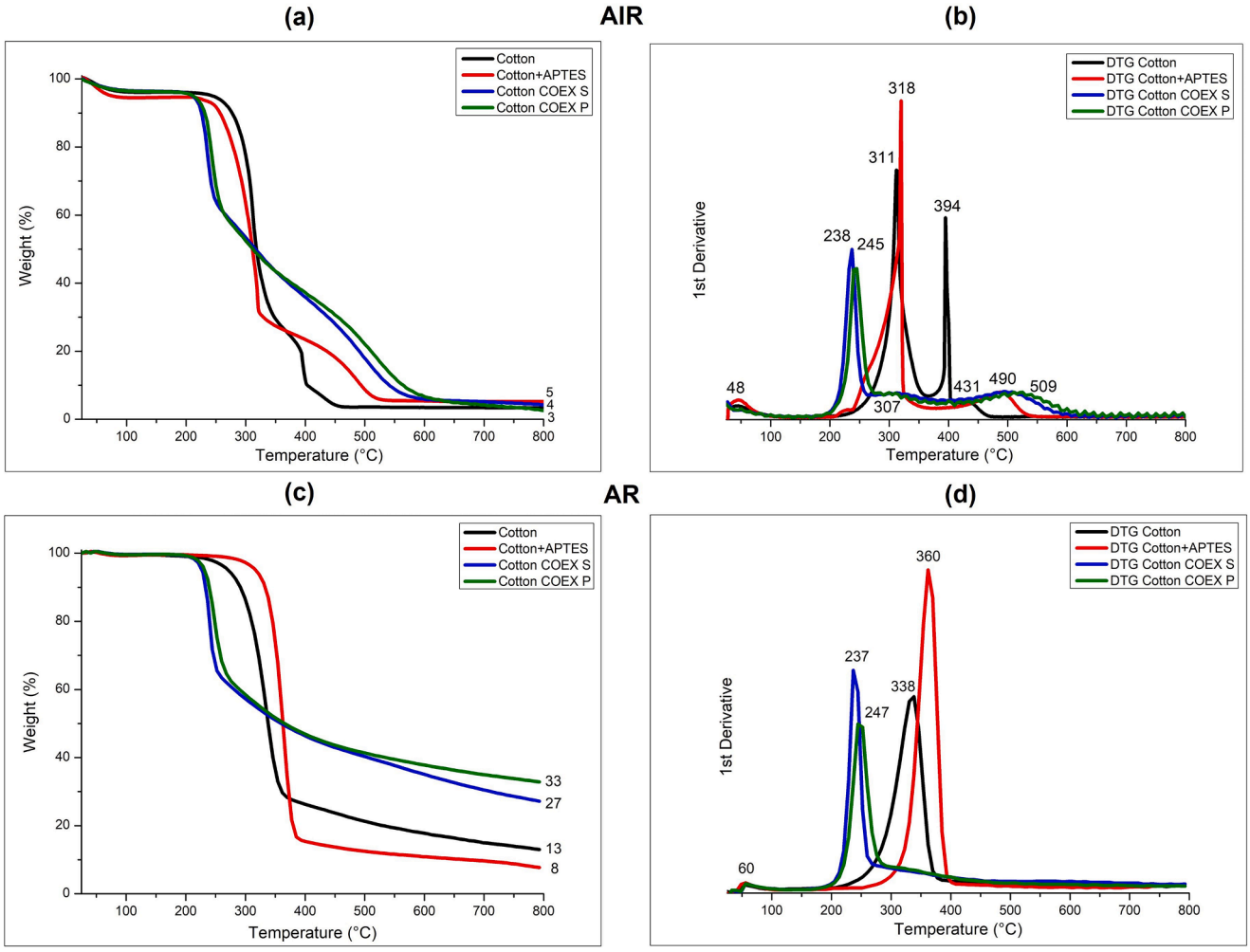

Fig. 5. TG and DTG curves comparison of unmodified and modified cotton fibers done in air (a,b) and argon (c,d).

Table 1
Thermal stability determined by TGA of unmodified and modified cotton fibers.

Sample	TGA in Air					TGA in Argon				
	T_5 (°C)	T_{10} (°C)	T_{50} (°C)	$T_{max\ deg}$ (°C)	Residue (%)	T_5 (°C)	T_{10} (°C)	T_{50} (°C)	$T_{max\ deg}$ (°C)	Residue (%)
Cotton	245	278	318	311/397/434	3	270	297	338	338	13
Cotton+APTES	80	251	312	318/490	5	315	335	365	360	8
Cotton COEX S	212	227	317	238/307/509	4	230	235	354	237	27
Cotton COEX P	211	235	312	245/307/509	4	230	240	370	247	33

from hydroxyl groups [23–26]. Masking OH groups with silanization shifts these processes to higher temperatures.

On the contrary, the other two modified cotton fibers show an onset of the formation of gaseous products at lower temperature, but a relevant increase of the mass of char residue. The sulfation-phosphorylation processes change the mechanism of decomposition from depolymerization to dehydration, as confirmed by Py-GC/MS analysis described below. The resulting charring process lowers the production of flammable pyrolysis products (tar), improving flame retardancy.

Compared with the unmodified cotton fibers, phosphorylated samples displayed lowertemperature for the onset of decomposition, end degradation temperature, and temperature at the maximum degradation rate, as well as much higher residual weights at 800 °C, as also shown in Table 1. The phosphorylated fibers undergo a dehydration process at lower temperatures, generating a char residue with better thermal stability. This can be explained considering that the phosphate grafted onto the cotton fibers is thermally converted to phosphoric acid which can act as catalyst for the dehydration reaction. For the sulfated and phosphorylated cottons, the temperature and weight loss for the first decomposition process are the same under air and under argon, underlining that this is a dehydration process not affected by the presence of oxidants. Moreover, higher values of char content percentage are obtained for cotton fibers modified by sulfation and phosphorylation, indicating better flame retardancy with respect the untreated cotton fibers, and do not generate high quantities of volatile flammable (tar) products under argon atmosphere [27–32].

In this way, TG analyses allow to infer that sulphonated and phosphorylated cotton fibers have higher charring ability at higher temperatures, as known from the literature [20].

Furthermore, DSC measurements were also carried out to evaluate the thermal properties of the unmodified and modified cotton fibers. Fig. 6 reports the DSC curves, performed in nitrogen, obtained from the heating and cooling cycles.

The thermograms did not identify any exothermic peak in the temperature range analyzed, indicating that no crystallization occurred during the cooling. The DSC curves of the unmodified and modified cotton fibers show a broad endothermic peak at lower temperatures, between 62–74 °C, attributed to the desorption of the water molecules adsorbed onto the fibers surface.

Moreover, at higher temperatures an endothermic peak was found for the fibers modified by sulphation-phosphorylation methods, centered at 248 and 250 °C respectively, assigned to the dehydration of the cellulose content of the cotton fibers.

The unmodified cotton fibers and the fibers modified by APTES as silane coupling agent present the same significant peak shifts towards much higher temperatures, 345 and 361 °C, respectively, to underline that their thermal degradation occurs at higher temperature due to their higher thermal stability. The enthalpy of the endothermic peak for the APTES-treated cotton is very high, relative to the other cotton samples. This finding confirms the relevance of the depolymerization process with levoglucosan generation for this cotton sample, as noticed by Py-GC/MS analysis.

The results obtained by DSC analysis including relevant endothermic peaks due to degradation phenomena are summarized in Table 2.

Table 2
DSC data performed in nitrogen of unmodified and modified cotton fibers.

Sample	DSC in Nitrogen	
	T_{onset} (°C)	T_{deg} (°C)
Cotton	62	345
Cotton+APTES	70	361
Cotton COEX S	74	248
Cotton COEX P	71	250

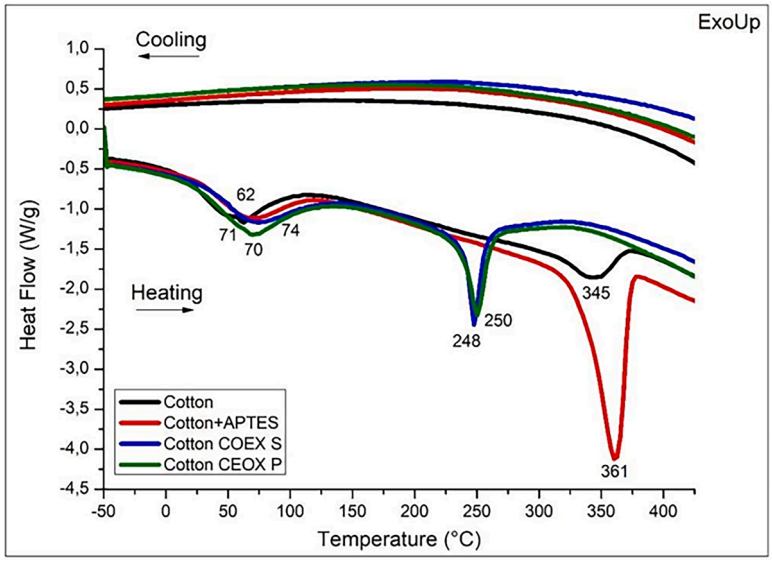

Fig. 6. DSC curves of unmodified and modified cotton fibers performed nitrogen.

4.3. Pyrolysis GC/MS study of cotton fibers

The decomposition of the untreated and modified cotton fibers was investigated using Py-GC/MS. Fig. 7 displays the total ion current (TIC) pyrograms of the decomposition products resulting from thermal degradation of the fibers at 600 °C under helium atmosphere. The pyrolysis products identified are presented in Table 3. Specifically, the pyrolysis of untreated cotton at 600 °C involves the formation of levoglucosan, a cellulose depolymerization product that results via intramolecular transglycosylation [27].

Additionally, a range of volatile dehydration products is produced, including 1,4:3,6-dianhydro-α-D-glucopyranose, furan derivatives, monoaromatic hydrocarbons (benzene, toluene), and low-molecular-weight oxygenates, such as hydroxyacetone, pyruvic aldehyde and butanedione. However, for all samples the main product is CO_2. The observed products are in accordance with prior studies that have investigated the pyrolysis behavior of cellulose and raw cotton at different temperatures [28–30].

Cellulose decomposition involves two main competing pathways: dehydration, which forms char, a carbonaceous material that is less flammable, and depolymerization, which leads to the production of levoglucosan, a specific compound resulting from the cleavage of the 1,4-glycosidic bonds in cellulose [27].

Levoglucosan undergoes fragmentation and dehydration during cellulose pyrolysis, yielding volatile substances and flammable tar that play a significant role in the speed of propagation of cotton combustion [31]. Hence, substances capable of reducing levoglucosan formation and consequently decreasing the production of volatile flammable compounds, are expected to act as flame retardant for cellulose fibers.

The pyrolysis of modified cotton fibers showed minor differences in terms of the type of pyrolytic products, but relevant differences in their relative amounts, underlining differences in the main pyrolysis processes. Concerning the products formed, in the pyrogram of cotton fibers modified with APTES, no silanes were found, only 5-(hydroxymethyl)-2-furancarboxaldehyde was identified as an additional product. In the pyrograms of COEX-modified cottons, sulfur dioxide (SO_2) and two nitrogen-containing compounds (2,5-dihydropyrrole and cinnoline) were identified.

The presence of these pyrolysis products is due to the cellulose sulphation process which involves the use of urea and ammonium sulphamate. The significant differences between the pyrograms of modified and unmodified cotton fibers are in the peak intensities, reflecting different product yields and pyrolysis pathways. A quantitative assessment of the pyrolysis products is reported in Table 4 and Fig. 8.

To assess the pyrolysis product yields, calibration curves were built for the main pyrolysis products: CO_2, benzene, phenol, pyruvic aldehyde, 2,3-butanedione, hydroxyacetone, butanedial, 2-furancarboxaldehyde, 1,4:3,6-dianhydro-α-D-glucopyranose, and levoglucosan.

The CO_2 calibration curve was obtained by injecting a known volume of pure CO_2 gas directly into the gas chromatograph. The char production was estimated from TG data, subtracting the amount of the residue at 800 °C in air from the residue at 800 °C under argon (data from Table 1).

The sum of identified products ranges from 49 % (APTES treated cotton) to 67 % (raw cotton). The balance can be due to other very volatile products, mainly water, CO and H_2.

Based on the product yields, different pyrolysis pathways can be distinguished for each type of cotton fibers.

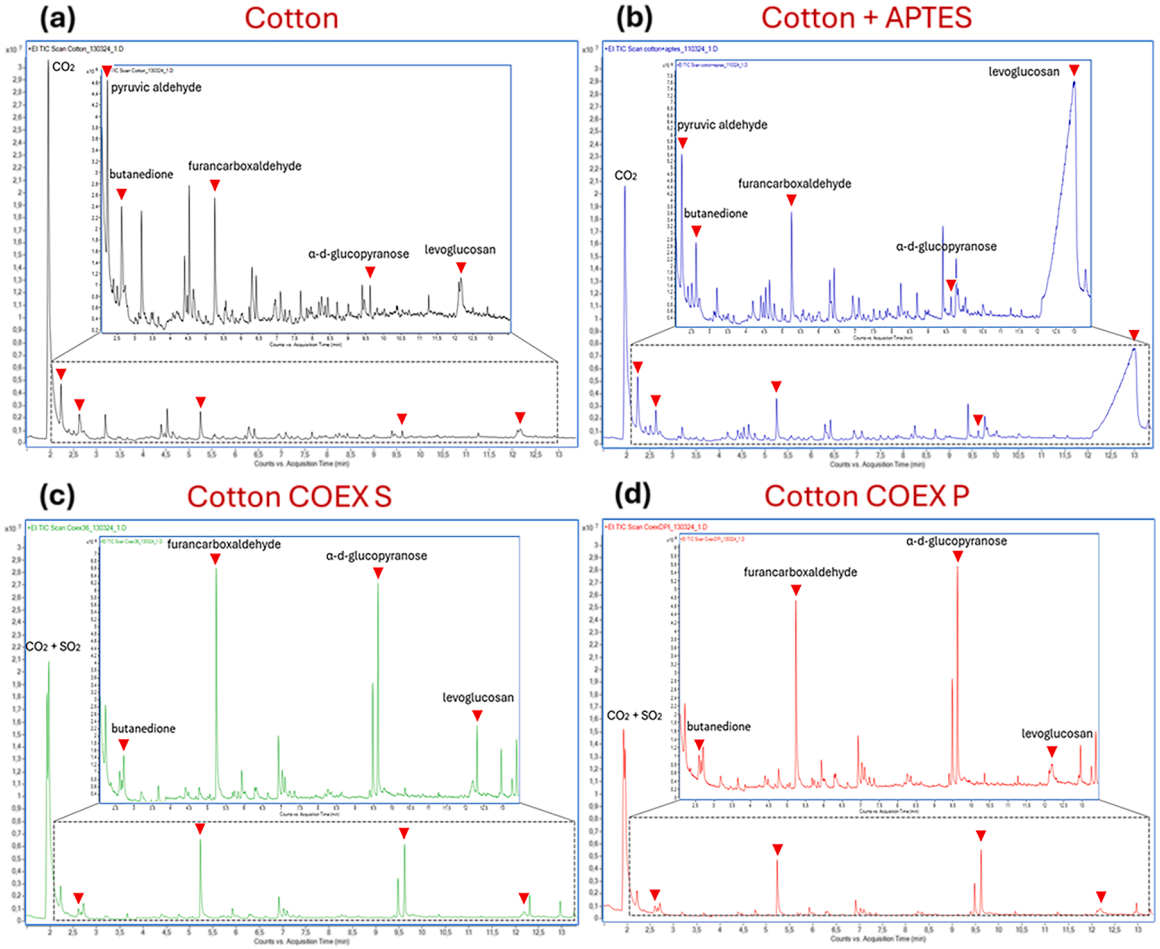

Fig. 7. Total Ion Chromatogram of the pyrolysis products at 600 °C of unmodified and modified cotton fibers.

Table 3
Identification of the main pyrolysis products from unmodified and modified cotton fibers.

Main Pyrolytic Products	Molecular formula	Retention time (min)	Nominal Mass	Cotton Peak Area%	Cotton+ APTES Peak Area%	Cotton COEX S Peak Area%	Cotton COEX P Peak Area%
carbon dioxide	CO_2	1,9	44	74,5	29,1	53,7	58,8
sulfur dioxide	SO_2	2,0	64	–	–	13,7	6,8
2,5-dihydropyrrole	C_4H_7N	2,2	68	–	–	4,5	5,0
pyruvic aldehyde	$C_3H_4O_2$	2,2	72	4,2	3,5	–	–
2,3-butanedione	$C_4H_6O_2$	2,6	86	3,5	1,2	1,1	1,2
3-methyl furan	C_5H_6O	2,7	82	1,3	1,2	1,2	1,2
hydroxyacetone	$C_3H_6O_2$	3,2	74	2,2	0,5	–	–
benzene	C_6H_6	3,2	78	0,6	0,3	0,8	0,7
2,5-dimethyl-furan	C_6H_8O	3,7	96	–	–	0,6	0,6
toluene	C_7H_8	4,4	92	1,7	0,5	0,5	0,7
butanedial	$C_4H_6O_2$	4,5	86	3,2	0,7	–	–
(2H) 2-furanone	$C_4H_4O_2$	4,8	84	0,4	0,5	0,7	1,1
2-furancarboxaldehyde	$C_5H_4O_2$	5,3	96	4,0	2,3	8,7	8,5
5-methyl-2(3H)-furanone	$C_5H_6O_2$	6,4	98	0,9	1,0	–	–
5-methyl-2-furancarboxaldehyde	$C_6H_6O_2$	7,0	110	1,2	0,8	2,0	2,5
cinnoline	$C_8H_6N_2$	9,5	158	–	–	3,8	4,4
1,4:3,6-dianhydro-α-D-glucopyranose	$C_6H_8O_4$	9,6	144	0,7	0,3	6,1	7,7
5-(hydroxymethyl)−2-furancarboxaldehyde	$C_6H_6O_3$	9,8	126	–	1,1	–	–
levoglucosan	$C_6H_{10}O_5$	12,2	162	1,8	57	0,7	0,8
2,4-di-tert-butylphenol	$C_{14}H_{22}O$	12,3	206	–	–	1,9	–

Table 4
Yields of pyrolysis products determined by Py-GC/MS.

Pyrolysis products	Cotton Yields %	Cotton+APTES Yields%	Cotton COEX P Yields%	Cotton COEX S Yields%
carbon dioxide	55	37	25	32
benzene	0,03	0,02	0,03	0,04
pyruvic aldehyde	0,52	0,71	–	–
2,3-butanedione	0,24	0,14	0,02	0,02
hydroxyacetone	0,31	0,11	–	–
butanedial	0,18	0,05	–	–
2-furancarboxaldehyde	0,18	0,31	0,54	0,74
1,4:3,6-dianhydro-α-D-glucopyranose	0,07	0,05	0,30	0,34
levoglucosan	0,04	6,7	0,01	0,07
Char	10	4	28	24
Total identified	67	49	54	57

Fig. 9 schematically summarizes the changes in the thermal decomposition mechanisms of the modified and unmodified cotton fibers, and the main degradation products.

In the case of unmodified cotton fibers, a low quantity of levoglucosan and volatile tar products was observed. The char residue amounts to 10 % of the initial cotton mass and high amount of CO_2 was detected, suggesting a high conversion of organic matter through decarboxylation and moderate charring to the ultimate decomposition product.

In contrast, APTES-modified cotton fibers exhibited a predominant production of levoglucosan, a significant decrease of CO_2 evolution and char residue, with respect to the other samples.

The modification with silane favors cellulose depolymerization over dehydration, leading to a nearly complete gasification of the cotton (see also TGA data). The high depolymerization yield to levoglucosan is due essentially to: i - masking of the cellulose hydroxyl groups with silane, hindering dehydration at 250–300 °C and favoring depolymerization [28,31]; ii - the silanization process involves a chemical treatment including a series of washes of the raw cotton resulting in the removal of inorganic salts, according to Nam et al. [28], the inorganic salts like potassium, calcium, magnesium and iron oxides, present in small percentages (1 %) in raw cotton catalyze dehydration reactions during pyrolysis, limiting levoglucosan yield and subsequently hinder the formation of flammable tar; iii - APTES -modified cotton is subjected to a treatment with strong bases: it is reported that acid-base catalysis increases the cellulose pyrolytic depolymerization to levoglucosan [32].

Regarding COEX-modified cottons, a predominance of dehydration products and less formation of CO_2 and low-molecular-weight volatiles compared to the unmodified and APTES modified cotton can be observed.

The sulphation-phosphorylation process is an effective flame retardant because it reduces levoglucosan formation and promotes dehydration to char at temperatures under 300 °C, thus favoring carbonization over conversion to levoglucosan and tar.

Among the two COEX cottons, some differences were found. On one hand, the peak area of SO_2 in COEX S was greater than that of COEX P, indicating a higher level of sulphation, consistent with SEM-EDS analysis. On the other hand, CO_2, levoglucosan, and furancarboxaldehyde emission factor were higher in COEX S in comparison to COEX P.

Therefore, a slight decrease of flame-retardant action for COEX S modification can be supposed, due to a lower presence of phosphonic groups compared to COEX P fiber. This underlines the importance of phosphonic group concentration in influencing flame-retardant properties within these fiber modifications, as reported in literature.

4.4. Wettability of cotton fibers

Finally, contact angle measurements with water were done to determine the wettability of the cotton fibers before and after the chemical modifications. Fig. 10 reports the water droplets behavior of cotton fibers before and after modifying. The raw cotton fibers show a wettability close to 125.4 ± 6.1 °, certainly higher than 90° which is more hydrophobic, due to the intrinsic characteristics of the cotton chemical structure, as well-known from the literature [21].

The fibers functionalized with APTES reveal contact angle values lower than the unmodified ones (118.0 ± 8.9) to underline that the presence of silane grafted onto the cotton fibers surface can induce a slight increase of their hydrophobicity. As visible, the water droplets maintained almost perfect spheres, without wetting the fibers. This hydrophobic property is mainly due to the amino groups of APTES which are bonded together with the hydroxyl groups through hydrogen bonding onto the fibers surface after the silanization reaction with APTES [21]. A different behavior can be observed for cotton fibers chemically modified by sulphation-phosphorylation methods.

Looking at the pictures reported in Fig. 10, it is noteworthy that it was not possible to determine the water contact angles of the fibers modified by sulphation-phosphorylation process, because of their very high hydrophilicity. In fact, the water droplets were immediately

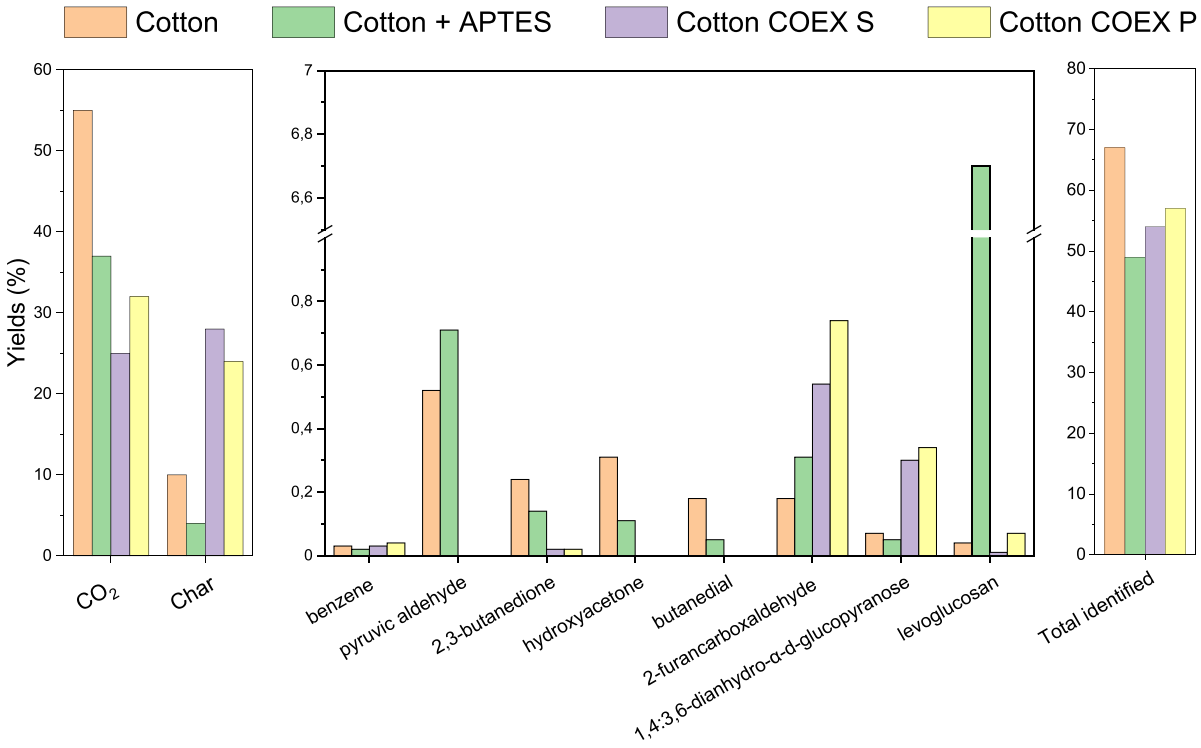

Fig. 8. Yields (%) of pyrolysis products from unmodified and modified cotton fibers.

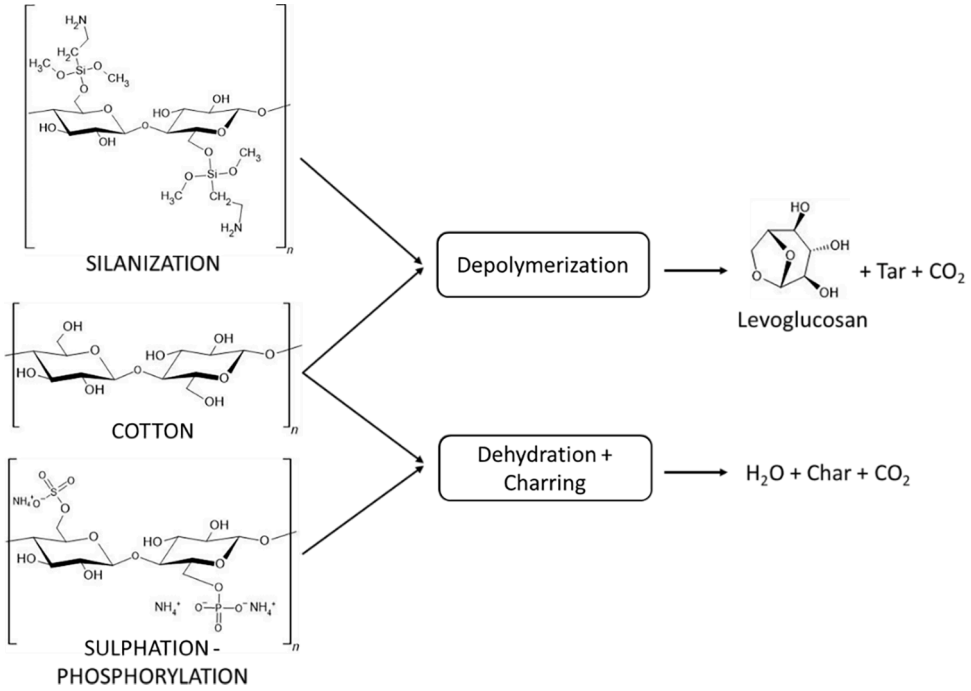

Fig. 9. Pyrolysis pathways for different types of cotton fibers.

absorbed by the cotton fibers. This can be probably caused by the process employed for the modification, which introduced onto the fiber's surfaces sulphonated groups, resulting in a relatively more hydrophilic surface than the original cotton fibers surface [10,11].

5. Conclusions

The present paper highlights complementary information on the thermal behavior and the decomposition products of cotton fibers functionalized by using different modification processes, involving conventional silanization with APTES and an innovative patented sulphation-phosphorylation method to obtain cotton fibers with

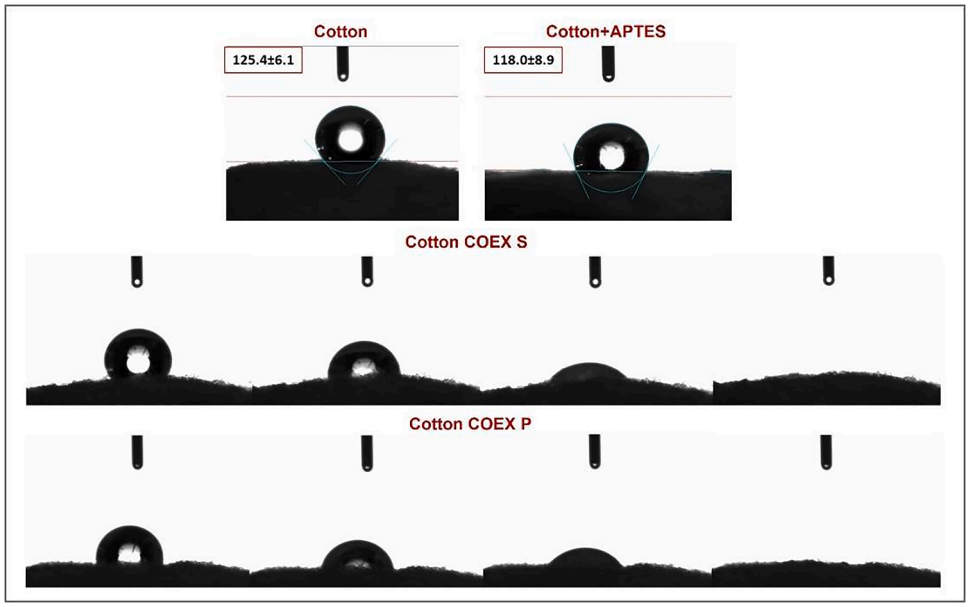

Fig. 10. Water droplets behavior of unmodified and modified cotton fibers.

improved final properties.

Combination of TGA, DSC, and Py-GC/MS studies on the properties and thermal behavior of treated cotton fibers allowed to draw important conclusions on the effect of the different surface modification treatments on the thermal decomposition products of cotton fibers. TGA measurements revealed that the silanization process influences the degradation of the cellulose fraction of the cotton fibers.

The APTES silanization treatment hinders the dehydration of cotton fibers in the 250–300 °C interval blocking the hydroxyl groups of the cellulose chain. This leads to very high yields for the depolymerization process around 360 °C, with a relevant production of levoglucosan and very low yields in residual char. However, due to the high yield in volatile flammable decomposition products, the fire resistance is negatively affected. Moreover, if the depolymerization to levoglucosan is pursued for conversion to liquid fuels, silanization process can improve the process yield.

On the other hand, the sulfated-phosphorylated cotton fibers show a completely different behavior.

TGA show a decrease of the onset temperature of the first mass loss (cellulose dehydration), but an increase of the mass of char residue. This new process radically changes the mechanism of decomposition from depolymerization to dehydration, as confirmed by Py-GC/MS analysis. In fact, surface phosphate and sulfate catalyze the dehydration processes, leading to a relevant char formation yield and suppressing the formation of volatile products and CO_2. This behavior greatly improves the flame retardancy of the cotton fibers.

SEM and EDS analyses were also performed to study the effect of the different modification reactions onto the cotton fibers surface, detecting the presence of silicon for the fibers silanized with APTES, sulfur and phosphorous for the cotton fibers modified with the novel sulphation-phosphorylation process. Water contact angle measurements were also done to evaluate the effect of the fibers surface modification on their hydrophilicity and hydrophobicity, evidencing that the modification with APTES induces a slight increase of their hydrophobicity due to the silane grafted onto the cotton fibers surface. On the contrary, the cotton fibers modified by sulphation-phosphorylation process revealed very high hydrophilicity due to the presence of S and P on their surfaces. These findings together with the thermal decomposition temperatures, weight losses, and potential reactions of pyrolysis as well as the resulted fragments identified put in evidence the mechanisms of flame-retardant of the novel cotton fibers. This can open the way to the use of cotton fibers in many industrial fields where the flame retardancy is strictly required, such as biomaterials design, oil recovery, textiles, and transportation.

Funding

This study was carried out within the Ministerial Decree n° 1062/2021 and received funding from the FSE REACT-EU - PON Ricerca e Innovazione 2014–2020. The authors also kindly acknowledge Piedmont Region for funding, through Bando LR34/2004 – D.D. n° 409 del 02/11/2021 (2021–2024) "Study and Development of ecological and low particulate emission braking materials for automotive applications".

CRediT authorship contribution statement

Mattia Isola: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Giovanna Colucci:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Aleandro Diana:** Formal analysis, Data curation. **Agusti Sin:** Supervision, Resources, Project administration, Funding acquisition. **Alberto Tonani:** Investigation, Formal analysis. **Valter Maurino:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

[1] A. Karimah, M. Rasyidur Ridho, S. Sofyan Munawar, I. Yusup Amin, R. Damayanti, M. Adly Rahandi Lubis, A. Peni Wulandari, A comprehensive review on natural

fibers: technological and socio-economical aspects, Polymers 13 (2021) 4280, https://doi.org/10.3390/polym13244280 (Basel).
[2] A. Karimah, M. Rasyidur Ridho, S. Sofyan Munawar, D. Sudarwoko Adi, Ismadi, R. Damayanti, B. Subiyanto, W. Fatriasari, A. Fudholi, A review on natural fibers for development of eco-friendly bio-composite: characteristics, and utilizations, J. Mater. Res. Technol. 13 (2021) 2442–2458, https://doi.org/10.1016/j.jmrt.2021.06.014.
[3] L. Ranakoti, M. Pokhriyal, A. Kumar, Natural fibers and biopolymers characterization: a future potential composite material, J. Mech. Eng. 68 (2018) 33–50, https://doi.org/10.2478/scjme-2018-0004.
[4] V.K. Thakur, A.S. Singha, M.K. Thakur, Biopolymers based green composites: mechanical, thermal and physico-chemical characterization, J. Polym. Environ. 20 (2012) 412–421, https://doi.org/10.1007/s10924-011-0389-y.
[5] Y. Xie, C.A.S. Hill, Z. Xiao, H. Militz, C. Mai, Silane coupling agents used for natural fiber/polymer composites: a review, Compos. Part A 41 (2010) 806–819, https://doi.org/10.1016/j.compositesa.2010.03.005.
[6] S. Liu, H. Ye, Y. Zhou, J. Zhao, Hydrolytic co-condensation of phenyltriethoxysilane with aminopropyltriethoxysilane in the presence of sodium dodecyl sulfate, Polym. J. 38 (3) (2006) 220–225.
[7] M. Abdelmouleh, S. Boufi, M.N. Belgacem, A.P. Duarte, A. Ben Salah, A. Gandini, Modification of cellulosic fibres with functionalised silanes: development of surface properties, Int. J. Adhes. Adhes. 24 (2004) 43–54.
[8] F. Zhou, G. Cheng, B. Jiang, Effect of silane treatment on microstructure of sisal fibers, Appl. Surf. Sci. 292 (2014) 806–812, https://doi.org/10.1016/j.apsusc.2013.12.054.
[9] A. Rachini, M. Le Troeder, C. Peyratout, A. Smith, Chemical modification of hemp fibers by silane coupling agents, J. Appl. Polym. Sci. 123 (2012) 601–610, https://doi.org/10.1002/app.
[10] B. Sun, M. Zhang, Q. Hou, R. Liu, T. Wu, C. Si, Further characterization of cellulose nanocrystal (CNC) preparation from sulfuric acid hydrolysis of cotton fibers, Cellulose 23 (2016) 439–450, https://doi.org/10.1007/s10570-015-0803-z.
[11] J. Song, Y. Jin, G. Fu, A. He, W. Fu, A facile approach toward surface sulfonation of natural cotton fibers through epoxy reaction, J. Appl. Polym. Sci. 124 (2012) 1744–1750, https://doi.org/10.1002/app.35180.
[12] D. Wang, J. Huang, H. Zhang, T.J. Gu, L. Li, Cotton Ti-IMAC: developing phosphorylated cotton as a novel platform for phosphopeptide enrichment, Appl. Mater. Interfaces 15 (41) (2023) 47893–47901, https://doi.org/10.1021/acsami.3c08697.
[13] R. Solovov, A. Perevoznikova, A. Seliverstov, A. Shapagin, A. Fedoseev, V. Milyutin, B. Ershov, Physicochemical and sorptive properties of a phosphorylated mercerized cotton fabric, Polymers 13 (2021) 3756, https://doi.org/10.3390/polym13213756 (Basel).
[14] F. Rol, C. Sillard, M. Bardet, J. Reddy Yarava, L. Emsley, Cellulose phosphorylation comparison and analysis of phosphorate position on cellulose fibers, Carbohydr. Polym. 229 (2020) 115294, https://doi.org/10.1016/j.carbpol.2019.115294.
[15] X.L. Jiang, R.C. Tang, Phosphorylation of kapok fiber with phytic acid for enhanced flame retardancy, Int. J. Mol. Sci. 23 (2022) 14950, https://doi.org/10.3390/ijms232314950.
[16] E.J. Blanchard, E. Graves, Phosphorylation of cellulose with some phosphonic acid derivatives, Text. Res. J. 73 (1) (2003) 22–26, https://doi.org/10.1177/004051750307300104.
[17] Tonani, A., Novello, A., Sirna, C., Giannatempo, S. (Inventors), Torcitura padana SpA and Zanolo SpA (Proprietors), Cellulose Substrate with Anti-Flame Properties and Relative Production Method, European Patent EP 3 030 583 B1, 15/06/2016.
[18] E. Conca, M. Malandrino, A. Diana, O. Abollino, A. Giacomino, R. Bartrolí, T. Moreno, X. Querol, F. Amato, Methods for elemental analysis of size-resolved PM samples collected on aluminium foils: results of an intercomparison exercise, Molecules 27 (2022) 7442, https://doi.org/10.3390/molecules27217442.
[19] N.D. Alharbi, H.H. Amer, N.A. El-Zaher, O.W. Guirguis, Development and characterization of cotton fabrics by dipping in solutions of chitosan and ZnO-nanoparticles as promising environmentally friendly reinforcements for polymer composites, Polym. Polym. Compos. 30 (2022) 1–12, https://doi.org/10.1177/09673911221148826.
[20] Z. He, S. Nam, D.D. Fang, H.N. Cheng, J. He, Surface and thermal characterization of cotton fibers of phenotypes differing in fiber length, Polymers 13 (2021) 994, https://doi.org/10.3390/polym13070994 (Basel).
[21] H.N. Chenga, A. Biswas, Chemical modification of cotton-based natural materials: products from carboxymethylation, Carbohydr. Polym. 84 (2011) 1004–1010.
[22] R. De Silva, N. Byrne, Utilization of cotton waste for regenerated cellulose fibres: influence of degree of polymerization on mechanical properties, Carbohydr. Polym. 174 (2017) 89–94, https://doi.org/10.1016/j.carbpol.2017.06.042.
[23] R.H. Blas-Sevillano, T. Veramendi, B. La Torre, C.E. Velezmoro-Sánchez, A.I. Oliva, M.E. Mena-Martínez, W.A. Herrera-Kao, J. Uribe-Calderon, J.M. Cervantes-Uc, Physicochemical characterization of several types of naturally colored cotton fibers from Peru, Carbohydr. Polym. 197 (2018) 246, https://doi.org/10.1016/j.carbpol.2018.06.006. –2.
[24] P. Zhu, S. Sui, B. Wang, K. Sun, G. Sun, A study of pyrolysis and pyrolysis products of flame-retardant cotton fabrics by DSC, TGA, and PY–GC–MS. J, Anal. Appl. Pyrolysis 71 (2004) 645–655, https://doi.org/10.1016/j.jaap.2003.09.005.
[25] G. Dorez, L. Ferry, R. Sonnier, A. Taguet, J.M. Lopez-Cuesta, Effect of cellulose, hemicellulose and lignin contents on pyrolysis and combustion of natural fibers, J. Anal. Appl. Pyrolysis. 107 (2014) 323–331, https://doi.org/10.1016/j.jaap.2014.03.017.
[26] E. Jakab, E. Meszaros, J. Borsa, Effect of slight chemical modification on the pyrolysis behavior of cellulose fibers, J. Anal. Appl. Pyrolysis. 87 (2010) 117–123, https://doi.org/10.1016/j.jaap.2009.10.012.
[27] X. Zhanga, W. Yanga, C. Dong, Levoglucosan formation mechanisms during cellulose pyrolysis, J. Anal. Appl. Pyrolysis. 104 (2013) 19–27, https://doi.org/10.1016/j.jaap.2013.09.015.
[28] S. Nam, B.D. Condon, Y. Liu, Q. He, Natural resistance of raw cotton fiber to heat evidenced by the suppressed depolymerization of cellulose, Polym. Degrad. Stab. 138 (2017) 133e141, https://doi.org/10.1016/j.polymdegradstab.2017.03.005.
[29] Q. Lu, B. Hu, Z. Zhang, Y. Wu, M. Cui, D. Liu, C. Dong, Y. Yang, Mechanism of cellulose fast pyrolysis: the role of characteristic chain ends and dehydrated units, Combust. Flame 198 (2018) 267–277, https://doi.org/10.1016/j.combustflame.2018.09.025.
[30] D. Chena, K. Cen, X. Zhuang, Z. Gan, J. Zhou, Y. Zhang, H. Zhang, Insight into biomass pyrolysis mechanism based on cellulose, hemicellulose, and lignin, Combust. Flame 242 (2022) 112142, https://doi.org/10.1016/j.combustflame.2022.112142.
[31] L. Jiang, J. Luo, F. Xu, L. Qian, Y. Wang, H. Li, Z. Fang, High yield production of levoglucosan via catalytic pyrolysis of cellulose at low temperature, Fuel 323 (2022) 124369, https://doi.org/10.1016/j.fuel.2022.124369.
[32] S. Maduskar, V. Maliekkal, M. Neurock, P.J. Dauenhauer, On the yield of levoglucosan from cellulose pyrolysis, ACS Sustain. Chem. Eng. 6 (2018) 7017–7025, https://doi.org/10.1021/acssuschemeng.8b00853.